Toxicity and Fire Hazards Associated With Shipboard Materials

Contributed Articles
From Invited Specialists
at
Naval Research Laboratory
Washington, D.C.

Naval Ordnance Laboratory White Oak, Silver Spring, Maryland

> Naval Weapons Center China Lake, California

September 18, 1967



19970728 166

APPROVED FOR PUBLIC RELEASE - DISTRIBUTION UNLIMITED

THE TREE TO SE

NAVAL RESEARCH LABORATORY Washington, D.C.

Toxicity and Fire Hazards Associated with Shipboard Materials

Prepared by Contributed Articles
from invited Specialists at
the Naval Research Laboratory, Washington, D. C.,
the Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland,
and the Naval Weapons Center, China Lake, California

Organized and Edited at the Request of the Chief of Naval Research by Dr. W. A. Zisman, NRL, Washington, D. C. Submitted 18 September 1967

Table of Contents

Section	I.	Introduction, by Dr. W. A. Zisman, Superintendent, Chemistry Division, Code 6100, Naval Research Laboratory, Washington, D. C.	1
Section		Ignition and Flammability Hazards Associated with Fuels, Oils and Solvents on Surface Vessels, by Dr. H. W. Carhart and Dr. W. A. Affens, Code 6180, Naval Research Laboratory, Washington, D. C.	13
Section	III.	Hazards Arising from Fires on Shipboard From Organic Materials Such as Paints, Plastics, and Insulating Materials, by Dr. A. L. Alexander and Mr. J. E. Cowling, Code 6120, Naval Research Laboratory, Washington, D. C.	41
Section	IV.	Shipboard Fire Hazards of Pyrotechnics and Explosives, by Dr. J. E. Ablard, Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland	59
Section	v.	Fire Hazards of Propellants, Explosives and Incendiaries on Shipboard, by Ad Hoc Committee, Dr. A. S. Gordon, Coordinator, Naval Weapons Center, China Lake, California	69
Section	VI.	Shipboard Fire Fighting Methods, Equipment and Materials, by Dr. R. L. Tuve and Mr. H. P. Peterson, Code 6040, Naval Research Laboratory, Washington, D. C.	77
Section	VII.	Naval Oxygen Breathing Apparatus (OBA), by Mr. R. R. Miller, Code 6130, Naval Research Laboratory, Washington, D. C.	95
Section	VIII.	Toxicity Aspects and Application of the Naval Protective Gas Mask to Shipboard Fires, by Dr. E. A. Ramskill, Code 6140, Naval Research Laboratory, Washington, D. C.	103

Section I. Introduction

by Dr. W. A. Zisman, Code 6100 Naval Research Laboratory Washington, D. C.

Origin and Purpose of This Report

- 1. This report originated from a request by the Chief of Naval Research of 3 August 1967 to the Director of the Naval Research Laboratory (see Appendix I). The task of selecting experts in the appropriate fields and organizing the requested report was turned over to the Chemistry Division Superintendent (Code 6100) who, therefore, has planned, edited and produced the report with the help of cooperating scientists and engineers from the three Naval Laboratories indicated in the Table of Contents. The need for a survey report on the "state of the art" with respect to "Toxicity and Fire Hazards Associated with Shipboard Materials" has long been evident. A series of disastrous fires on surface vessels of the Navy, starting from the terrible damage suffered by the BENJAMIN FRANKLIN in World War II and ending most recently in 1967 with the FORRESTAL, has focused rapidly increasing attention on the subject of fire prevention and fire hazards to the crew.
- 2. In the various Naval Commands and Laboratories and especially in the Fleet, fire hazards have been of much concern. However, rapid changes in the fighting equipment and weapons of the Navy have occurred since World War I, and the problems of keeping ahead in the arms race and of using new weapons and naval warfare concepts have monopolized funds as

well as R & D activities.

- 3. Of course, the search for better methods of fire fighting and of decreasing fire hazards are as old as civilization. Despite the fact that there has been widespread interest in both subjects, especially in certain industries, in the fire departments of larger cities, in the larger fire insurance companies, in various state and federal agencies, and in the merchant marines of every nation, there are many possibilities not yet adequately explored. However, research at NRL over the past 20 years has revealed many chemical and engineering possibilities and problems of fighting fires and of decreasing fire hazards. Especially limiting to interested scientists and engineers has been the inadequate and discontinuous support for such research.
- 4. On naval surface ships, even in peacetime, the fire hazards are potentially more serious than on merchant ships or in land civilian installations. Furthermore, acceptable fire-fighting facilities and methods are different of necessity. Fire on board a naval ship can initiate a disaster so serious that the economic justifications for specific

choices of materials of construction or fire-fighting methods can be entirely different than those guiding designers and builders of merchant ships or of civilian land establishments. For example, we know of no other activity on the sea, or on land, where the possibilities of ignition, fire, and explosion are so numerous and potentially disastrous as those existing on board a modern, large, aircraft carrier. Of course, the possibilities become more numerous when the carrier is about to launch a major "air strike" (as in the case of the FORRESTAL) or where it is under air attack (as in the case of the BENJAMIN FRANKLIN).

- 5. Because of modest rate of progress in fire-fighting methods in civilian life and in the merchant marine, all of the technical information and guidance presented in this report had to be obtained from within the Navy's own technical establishments. Fortunately, within several large naval laboratories, there had accumulated from past research, development, and trouble-shooting experience with the Fleet, a considerable body of highly relevant technical "know-how" and ideas. Because of this situation, we were able to assemble the following report.
- 6. All designs for naval ships have always represented the result of many compromises between numerous and conflicting requirements, such as those relating to optimum ship speed, maximum range of operations, ability to execute many kinds of maneuvers and missions during combat, reasonable comfort, health and safety for the crew, the need to use available materials of construction, and reasonable costs of construction and

maintenance. These compromises appear to be especially numerous, conflicting, and difficult to make in the design of modern, large, aircraft carriers.

The same could be said to varying degrees about many other ships where space
limitations and special missions also bring serious problems, e.g., destroyers,
cruisers, and tankers.

- 7. As the fire, explosion, and toxic hazards in submarines involve many factors and restraints peculiar to such ships, especially during deep submersion, such hazards in submarines need to be discussed in a separate report. In certain respects, the hazards in submersibles have been given much more attention than surface ships, and this is especially true of the atmospheric pollution and related toxicity problems. As we believe that the most dangerous fire hazards in the Fleet exist today in aircraft carriers, special emphasis will be given in each section of this report to these problems aboard carriers.
- 8. This report was prepared recognizing that to gather and condense all available Naval research, development, and engineering knowledge on fire, ignition, and toxic hazards of ships together with the associated recommendations from the Navy's many laboratories and engineering establishments, would take at least a year to compile. But the fire hazard problem is of so much concern to the government as well as the public that it was decided to answer the request of the Chief of O.N.R. (Appendix I) by gathering together the technical guidance already available from a group

of experts who, in the judgment of the Editor, were the best informed Naval engineers and scientists in their fields by virtue of their research and development experience, their past accomplishments, and their intimate knowledge of relevant activities in the Navy (or for the Navy) in their own fields of competence. The resulting reviews by these authors of the state of knowledge along with their recommendations for future action are believed so valuable and up to date that they should prove helpful and timely to many fellow workers and administrators in the Department of the Navy. Many recommendations will bear study by the other services of the Department of Defense. As indicated below, there are a few other sources of information within the Navy we need to draw upon to fill in the picture as completely as possible; we propose to submit additional material as a supplement to this report as soon as possible. Nevertheless, the discussions and recommendations presented here from Navy's R & D laboratories is so reliable, well informed, and nearly complete that it deserves early attention by those in the Navy Department and Department of Defense who are responsible for planning, budgeting, and action.

Lack of Reliable Data on Toxicity Hazards on Shipboard

9. The subject of toxicity, especially the exposure of men in closed atmospheres, has been largely neglected until Navy nuclear submarines and later NASA space vehicles required the effort. Only in the past decade has enough reliable research been done, especially in the effort of the Naval Research Laboratory on nuclear submarine atmospheric

pollution and control. We have given solutions to submarine problems which have permitted building workable systems, and we can point to needed areas of R & D which are highly relevant. Much of the earlier information on the safe toxic limits of chemicals was obtained after years of debate between many toxicologists; unfortunately, the resulting permissive limits for atmospheric contamination relate only to exposure of men to an atmosphere at ordinary temperatures and pressures. This early information was obtained in major part to guide industry in protecting its workers under conditions of exposure of eight hours per day for five days per week.

- 10. The toxic hazards encountered during naval ship fires may involve exposures to special atmospheric pollution, and usually there is a more or less brief exposure to an atmosphere containing more than one toxic chemical at the same time (see Section VIII). Toxic hazards from fires on shipboard often arise under conditions during which the crew members are working frantically to combat the fire; many men are taxing human physical endurance beyond the limits commonly encountered in exposures to toxic materials in most industrial working conditions. There is reasonable doubt as to the applicability of much of the available toxicity data under such shipboard conditions. An adequate study of the toxic hazards on surface ships during normal operations and during fires will take a long time and will require a collection of much data by air sampling on shipboard in both closed and open spaces.
- 11. Appropriate collecting procedures and techniques for sampling the air under such conditions have been developed and much used by NRL during

ten years of investigations on the habitability of the nuclear submarine atmospheres as well as of the Mercury space capsules of NASA. An annual unclassified report of this work has been published for the past seven years. It is urged that a similar air-sampling program be initiated on surface ships, especially on aircraft carriers. It should commence with sampling of the air in many closed compartments as well as on deck areas under normal operating conditions at sea; subsequently, automatic sampling devices should be installed to collect air samples during wartime operations or fires.

- 12. In Section III of this report will be found recommendations for the collection of more laboratory data on the products evolved during overheating, or partial combustion, of a variety of solid materials used widely aboard naval vessels. Such an investigation needs to be started as soon as possible so that we can learn more about the toxic chemicals released in the atmosphere during shipboard fires. Much of the data needed are not available in the scientific or industrial literature or from industrial sources. Such an investigation should make evident any needed changes in materials used on board ships.
- 13. Despite the very limited amount of reliable information available on the amount and nature of the toxic chemicals in the ships' atmosphere during a fire, some important conclusions can be drawn about the causes of a significant proportion of the many deaths that have occurred during

past major naval shipboard fires. Specifically, reference is made to the all too numerous deaths which occurred from 24 to 48 hours after crew members have inhaled smoke while fighting a fire. The able discussion in Section VIII of this report is particularly alarming; early action is needed along the lines recommended therein to prevent many future deaths from pulmonary edema.

Fire, Explosion, and Toxic Hazards Arising from Stored Rockets

14. In Section IV from NOL, White Oak, Maryland, and Section V from NWC, China Lake, California, will be found condensed but valuable discussions of fire and explosion hazards aboard surface vessels arising from the presence there of explosives, pyrotechnics, rockets, and weapon arming and launching systems. Unfortunately, the Editor learned recently that information is available on fire and toxic hazards arising from stored rockets, such as Talos, Tartar and Terrier, and it will be necessary to review the investigations of such systems carried on the past eight years at the Naval Weapons Laboratory, Dahlgren, Virginia. If this information proves new and relevant, it will be sought and condensed into a supplementary report.

<u>Definitions of Short-, Intermediate-, and Long-Term Recommendations</u>

15. We have used in this report a uniform definition of each of the following terms; "short-term," "intermediate-term," and "long-term" recommendations. Such a breakdown of the recommendations should be helpful to all officials in the Navy Department who are concerned with decreasing

the fire, explosion, and toxic hazards aboard naval surface ships. By a short-term recommendation we mean one which is based on pertinent and existing technical know-how even though, to our knowledge, it is not yet in use on surface ships. Such recommendations need to be given early attention and action. Brief references are given wherever necessary to pertinent naval reports or publications or to any technical groups or codes in the Naval Systems Commands that we know are already concerned or involved in the proposed action. In short, the short-term recommendations emphasize the need for early changes in existing materials, specifications, procurements, equipment designs or redesigns, or personnel training.

- 16. By an <u>intermediate-term recommendation</u> we mean one dependent on the use of either available scientific and engineering know-how or some research and development which with a proper high priority could be put into naval practice in five years or less. Such a measure needs special ear-marking, because if approved, it would obviously require early priority, budgeting, engineering design, specifications, and procurement.
- 17. By a <u>long-term recommendation</u> we mean one which depends upon research to acquire necessary knowledge that does not exist. Such an effort would obviously require early and continuous funding of research for, possibly, five years or more. Under this heading, we include both highly relevant as well as "blue-sky" ideas.
 - 18. The recommendations in this report have been broken down into the above-defined three categories in order to help explain and justify to

the following people in the Navy Department and Department of Defense;

(i) those who must be informed of the need for justifying priorities and budgets on research and development, and (ii) those within the Naval Systems Commands who are responsible for related planning, designing, preparing specifications, training and instructions, and procurements. It is hoped that the need for each intermediate and long-term recommendation has been explained clearly in this report and that it has been placed in proper perspective relative to Naval shipboard and future design problems.

Readiness of the Naval Laboratories

19. The contents of the following seven sections of this report were all made available to the editor within one month after receipt of the request of Appendix I from the Chief of Naval Research. However, no one should assume that these technical discussions and recommendations represent a body of hastily-contrived explanations and suggestions. In every instance, each author has been involved deeply in the research and development activities in a naval laboratory on the subject he has discussed, and in every instance he has had a continuing interest and knowledge of activities in that field of R & D extending back from ten years ago to, in many instances, World War II days. In other words, each author has written from a full mind with a rich background concerning the R & D aspects of the problem with an authoritative knowledge of naval practice and experiences with the use of the equipment and materials discussed. The ability of this group of men to put such an authoritative and competent report together

so rapidly with such highly specific recommendations for short-, intermediate-, and long-term action is, indeed, a demonstration of the competence, high esprit de corps, and readiness of the scientists and engineers of the Navy's laboratories.

<u>Acknowledgements</u>

20. It is a pleasure to express the Editor's appreciation to, and admiration of, the authors of the following seven sections of this report. It is a noteworthy fact that the top command and the research administration of each of the three naval laboratories participating in this report agreed to allow their specialists to participate in this report-writing task with no more delay than was required for the Editor to make a telephone call to state the objective, expertise needed, and proposed organization of the report. Following that, a copy of the directive of Appendix I from the Chief of Naval Research was sent by air-mail. For this rapid reaction and wholehearted cooperation, the editor and the Director of the Naval Research Laboratory wish to record here their sincere thanks. The Editor's thanks are due to Mrs. Loretta P. Harding, Code 6100A, who typed this long report in a uniform format under most difficult circumstances, and also to Mrs. Bettye C. Foster, Code 6102A, Administrative Officer, Chemistry Division, for her efficient general support and liaison help within the five branches of the Naval Research Laboratory that contributed so effectively to this report.



DEPARTMENT OF THE NAVY OFFICE OF NAVAL RESEARCH WASHINGTON, D. C. 20360

IN REPLY REFER TO

3 August 1967

MEMORANDUM FOR DIRECTOR, NAVAL RESEARCH LABORATORY

Subj: Toxicity and fire hazards associated with shipboard materials

- 1. For some time the Navy has paid particular attention to materials used for construction, preservation and habitability going into our nuclear submarines to insure against undue fire and toxicity hazards. This attention to detail has resulted from the particular interest of the project managers responsible for construction and from the requirement for man to operate in closed environments for long periods of time.
- 2. The catastrophe on the ORISKANY and more recently that on the FORRESTAL indicate that the Navy might well direct its attention to the hazards of materials used in surface ships to a greater degree than here-tofore. Methods of combatting shipboard fires, once started, in both enclosed and open spaces, should be reviewed.
- 3. This subject is not necessarily a glamorous one, and capabilities within the Navy are not widespread. At the moment, much of the expertise would appear to rest in the Naval Research Laboratory.
- 4. It is requested that you prepare a "state of art" report that I can submit to ASN(R&D) that addresses itself to this general question. It should include a summary of fire and toxicity hazards associated with paints, coatings and other materials used in the construction, furnishings and equipment of our surface ships. A discussion of fire fighting methods and techniques should be included. In addition, the study should identify in-house capabilities in the Navy and include some mention of their activity. In order to complete this "situation" report, it would be well to describe how control of material installation is exercised with particular reference to the attention paid to the problems of fire and toxicity.
- 5. You should feel free to contact elements of the various Systems Commands whose equipment or installations may pose such hazards.
- 6. Would you give me an indication of the date by which such a report could be ready?

T. B. OWEN

Section II. Ignition and Flammability Hazards Associated with Fuels,
Oils and Solvents on Surface Vessels

by Dr. H. W. Carhart and Dr. W. A. Affens Naval Research Laboratory Washington, D. C.

Fire and Explosion Hazards

- 1. There is no more terrifying cry aboard ship than "Fire!" This is all the more true on naval vessels, and aircraft carriers in particular, because of their special and large cargoes of munitions, pyrotechnics, missile propellants, aircraft fuels, and the like. The very same flammability properties which make these materials so useful when properly controlled make them dangerous to life and property when out of hand.
- 2. Flammability, or the ability of a combustible to ignite and burn, depends on the nature and quantities of the three "sides" of the "Fire Triangle" (oxidant, ignition source and combustible). On a naval vessel, the most important oxidant is air, but liquid oxygen, hydrogen peroxide, chlorine, and the like, can also be present or be produced in certain parts of the ship. Ignition sources may be from open flames, sparks (from static electricity or from electric motors, high frequency discharges induced from radar, radio, etc.), hot gases or vapors or objects (spontaneous ignition), shock waves (from explosions, etc.), or from hypergolic ignition (propellants); they may be found almost anywhere aboard ships in one form or the other of sufficient energy to ignite a fire. For example, it has been demonstrated by NRL (1) that radio frequency arcs developed on aircraft parked on the flight deck of

an aircraft carrier can ignite flammable concentrations of fuel vapor. Current NRL research is investigating hazards from static electricity generated in fuel systems (2).

- 3. The most important and complex side of the Fire Triangle in a ship is the <u>combustible</u> or fuel, because of the large quantities on board, and because there are present so many varieties and forms. There are three important factors in the flammability of a combustible:
 - (a) Flammability Properties.

By the flammability properties we mean the combined chemical and physical properties which make one chemical compound more flammable than another, such as chemical reactivity, vapor pressure, flammability limits, heat of combustion, etc., which are the determining factors of ignitibility and flame propagation. Since liquid fuels must be in the vapor state to burn, a fuel with a higher vapor pressure (e.g., AvGas) would produce more vapor than one of lower pressure (e.g., JP-5). The concentration of vapor is also important in determining flammability, so that combustibles with broader flammability limits (JP-4 jet fuel, for example) are flammable over a wider tamperature range than those with narrow limits (JP-5 jet fuel, for example).

(b) Physical State.

The physical state of any combustible is of prime importance in determining its flammability properties. Vapors and gases are, in general, more flammable than liquids, which in turn are more flammable than solids. Thus, with increasing temperatures combustibles tend to become more flammable as they liquefy and/or vaporize. In addition to

tibles in the form of powders, droplets, or thin sheets are more flammable than in the bulk form, because the greater ratio of fuel area to its mass guarantees more intimate contact with the oxidizing agent—the air. In addition to flammability, the mobility of a substance is a factor in the propagation and spreading of fire. Burning solids tend to stay fixed whereas burning liquids may flow from place to place and spread the fire to combustibles in other areas. Combustible gases and liquid mists (3) tend to be explosive.

(c) Quantity.

The potential of a burning fuel to cause a fire disaster is a function not only of its flammability, but also the amount present. The importance of quantity can be illustrated by going from one extreme to another. It can be seen that a pint bottle of extremely flammable ethyl ether on the shelf of a pharmacy is not nearly as potentially disastrous as 2000-4000 gallons of the less flammable jet fuel stored in a single aircraft.

(d) Miscellaneous Flammability Factors.

Other factors which influence flammability hazards of materials include ambient temperature and pressure, location of the combustibles, whether the space in which they are located is confined or open, the existence, distribution and intensity of ventilation drafts or wind, the geometry of the locale in which fire initiates, and the nature of the surrounding materials.

Fire Danger to Personnel in Confined Spaces

4. Loss of life or injury resulting from fires may be caused by heat, pressure, toxic effects of carbon monoxide and other combustion products, anoxia, or to more than one of these. In confined spaces, these effects may be of surprising magnitude. For example, in the NASA Apollo-204 fire at Cape Kennedy on 27 January 1967, the burning of only four ounces of nylon (debris net) would have been enough to have ruptured the capsule, which occurred only about 20 seconds after the fire was believed to have started. Similarly, in the fatal fire at the Experimental Diving Unit on 16 February 1965 (in a manned high pressure chamber at the Washington Navy Yard), the indicated increases in pressure and temperature were calculated to be over 100 psi and 400°C respectively, all occurring in a few seconds, which would result from the burning of about one pound of cotton, the equivalent of a terry cloth bathrobe. A research project on ignition and combustion in unusual atmospheres was initiated at NRL as a result of this accident. Preliminary results have demonstrated the importance of oxygen concentration on ignition and burning rate (4).

Petroleum Fuels

5. From the standpoint of fire disaster potential on naval ships, the most important combustibles (because of quantity and flammability) are the petroleum fuels including jet fuels, gasoline, fuel oil, and the like. Besides the fire or explosion hazards of petroleum fuels, their vapors are toxic to human beings. The maximum permissible content of petroleum vapors for any compartment or tank which is to be entered by

persons has been fixed at 0.1 percent by volume which is the <u>lower toxic</u>

<u>limit</u> (5). The vapors of gasoline, diesel fuel, kerosene, etc., are

classified as "moderately toxic" (6), but in those cases where the fuel

contains higher proportions of benzene and/or other aromatics, the

toxicity increases greatly (7).

Hazards of Fuels and Other Liquid Combustibles Aboard Surface Ships

6. Aircraft carriers and tankers present the greatest hazards of all surface ships in that on them fires can readily lead to a catastrophe because of the tremendous quantities of readily combustible fuels and oils carried. Although other large surface craft, such as cruisers and destroyers, also carry petroleum fuels, ordnance, and other combustibles (such as mattresses, paper, paint, etc.) and do have fires, experience alone shows that they are not as prone to disaster from fire. Submarines, small surface vessels, dry cargo and other surface ships and shore installations also have their own fire hazards, again largely because of fuels and other combustibles. What applies to carriers and tankers also applies to them, but, because they don't carry as much flammable fuel, they do not present as great a potential for disaster.

Aircraft Carriers

7. A large aircraft carrier such as the USS FORRESTAL (CVA-59) has the following capacities for petroleum fuels:

Navy Special --2,500,000 gal. JP-5 (jet fuel)-1,500,000 gal. 115/145 AvGas -- 100,000 gal. Of the JP-5 supply, 100,000 gallons is set aside as a diesel fuel for use in auxiliary and emergency engines. (Sometimes diesel fuel itself is bought for this purpose.) Both Navy Special Fuel Oil and JP-5 are carried in tanks just inside the skin of the ship. The JP-5 is passed through clean-up stations (at ca. 250 gal/min) into four service tanks, from which aircraft are fueled (at a potential total flow of over 2000 gal/min) mostly on the flight deck, but also occasionally on the hangar deck. AvGas is stored in the armored part of the ship and is pumped by water displacement. Navy Special and JP-5 are not.

8. Aircraft carriers also carry other flammable petroleum products. On conventional aircraft carriers about 300 gallons of motor gasoline (MIL-G-3056), for use in small auxiliary engines and jeeps is stored in six 55-gal. steel drums on the fantail (so they can be jettisoned quickly in case of trouble). On the LPH's (helicopter landing platforms), motor gasoline is carried inside the armored part of the ship in a separate water-displacement system like that used for AvGas. hydraulic system of each of the main elevators contains 8000 gallons of triaryl phosphate, a much less flammable material than petroleum fluids. The hydraulic fluids used in the retracting gear for the steam catapults and for the jet blast deflectors and arresting gear are Hydrolubes (an NRL development during World War II), which are essentially glycol-water systems and are nonflammable in air (8). Other hydraulic systems on board use a variety of petroleum-base fluids (from 50 to 250 gal. each). Reserve stocks are normally stored in drums in special lockers (not in the "paint" lockers). When a high pressure leak occurs in a hydraulic

system, so that petroleum bil is spewed out in the form of a spray or mist, accumulation of such mists can yield highly explosive mixtures (9), especially if there is a delay in their being ignited (The USS BENNINGTON (CV-20) disaster in Narragansett Bay on 26 May 1954 was of this type.); or, if ignited immediately, they can generate a fire like an intense blowtorch (the principle of the home oil heating furnace). The steam turbine oil in the machinery spaces is essentially petroleum (2190 TEP), and several thousand gallons are stored in bulk in the engine rooms. Aircraft engine oils are stored in 5-gal cans on the hangar deck and are made from a petroleum base for reciprocating engines (type 1065) and for some jet engines (type 1010). Most jet engines now use a diester, triester, or tetraester-type oil (type MIL-L-23699), also an NRL-Navy development (10-12), but also combustible.

9. JP-4, a wide-cut gasoline type, is used in greater quantities than JP-5 by the military. It is used almost exclusively by the Air Force and also in some Navy shore stations. JP-4 is a much more flammable product than JP-5, with an unspecified flash point of around 0°F (the lower or lean flammability limit temperature). Its vapors form explosive mixtures in a closed container up to about 70°F (the upper or rich flammability limit temperature). For this reason, JP-4 is not allowed on board aircraft carriers. Indeed, JP-5, with a specified minimum flash point of 140°F, was designed specifically for carrier use as a much safer fuel, and NRL has been instrumental in keeping this value high for safety reasons. Information resulting from a current NRL research project in the Fuels Branch is assisting in the solution of this problem (13-16).

- 10. Generally, when a plane leaves a shore air station for later landing on an aircraft carrier, it is fueled with JP-5. The Navy still uses some JP-4 (Navy aircraft engines are qualified on both fuels.); however, if by chance a plane has JP-4 fuel in it, and lands on an aircraft carrier, and needs any kind of work on it, the JP-4 is jettisoned. Close attention is usually paid such a plane to minimize hazard.
- ll. Most fueling of aircraft is done on the flight deck, from hydrants along the catwalk with long hoses attached. Since both JP-5 and AvGas are used on aircraft carriers, in order to minimize using the wrong fuel, fueling stations for these two fuels are segregated on different parts of the ship. Fueling hoses for AvGas are noncollapsible, and fueling is performed overwing with conventional nozzles. JP-5 is fueled with collapsible hoses, underwing, under pressure with a special nozzle that attaches to a receptacle under the wing. Thus, the mixing of fuels is made difficult; nevertheless, spillage due to carelessness is not uncommon. Helicopters (now using JP-5 on aircraft carriers) are fueled either from above or below.
- 12. Flammable solvents, paint thinners, and other flammable liquids are stored in the "paint locker" because they are rightly considered as more hazardous than most solid combustibles. In as complex a structure as a ship, spilled fuels and other burning liquids pose a more difficult problem of control, because they run and spread into other areas whereas solids tend to stay put.

<u>Tankers</u>

13. Navy tankers (oilers) also carry large volumes of liquid combustibles. Only three products are carried on such ships, 115/145 AvGas, JP-5 and Navy Special Fuel Oil--usually simultaneously. Unfortunately from a hazard standpoint, the newer naval tankers, the AOE's, carry ammunition as well as fuels for transfer at sea. Such a mixed cargo is particularly hazardous, to say nothing of the vulnerability presented during transfer operations at sea, when both fuel and munitions are transferred simultaneously. AOE's have a capacity of 177,000 barrels of fuel (7,334,000 gallons), and a normal cargo consists of about 60% Navy Special, 36% JP-5 and 4% AvGas. The old fleet oilers (type T-2), which were used in World War II, carry only the three fuels with a maximum capacity of 125,000 barrels (5,250,000 gallons). Other fuels and oils needed and used on other Navy ships are preloaded in port. MSTS tankers carry all sorts of cargo, including aviation and motor gasoline and JP-4, but these are not intended for transfer to moving ships at sea.

Cruisers and Destroyers

14. In addition to the normal combustible solids, ordnance, solvents and Navy Special Fuel Oil, cruisers and destroyers also carry relatively small quantities of JP-5 used in helicopters which are fueled on deck, or are used in lieu of diesel fuel for auxiliary engines. These and other surface ships pose the more conventional hazard resulting from a multiplicity of combustibles associated with a large number of closely packed people in a complex structure full of machinery.

Handling

15. The transport, handling and use of petroleum products must always be considered as hazardous. This is particularly true on aircraft carriers during preparations for strike operations when planes are being fully loaded with fuel as rapidly as possible and are then jammed like sardines on the aft section of the flight deck (e.g., the FORRESTAL again). If there are 50 planes, averaging 3,000 gallons of fuel apiece, the flight deck would have on it 150,000 gallons of fuel (let alone ordnance) at a particularly critical and hectic time. The vulnerability of carriers at such times cannot be overlooked, nor can the periods of fuel transfers between ships at sea. However, the fact that the number of ship disasters has not been larger attests to the good discipline and control exercised in the transport, handling and use of such large volumes of highly combustible fluids, as well as to the effectiveness of the fire fighting and damage control parties.

Fire Hazards during Various Operations

16. The extent of fire hazard varies markedly with the activity of a ship. Much of what has been discussed herein deals with present day peace or limited wartime operations. But there are special hazards to consider during ship construction or repair and during all-out war. Hazard from fire during construction is high because of the large amount of combustibles present (wood in scaffolding, packing crates, trash, etc.), less efficient housekeeping (schedules to meet), high activity and larger numbers of people whose work enhances ignition sources (welding, etc.), and finally the fact that fire barriers are

not all installed. The USS CONSTELLATION (CVA-64) fire at the New York Naval Shipyard on 19 December 1960 is a good example of the hazard posed, in which conduits conveying closely packed bundles of electrically insulated wire (most of which was coated with polyethylene) served to carry fire and smoke from one ship compartment to another (see Section III). Fortunately, the fire was not worse because during that construction large quantities of fuels and munitions were still not on board.

17. Under full wartime conditions, a carrier has operational requirements imposed on it that make it particularly vulnerable to fire. This is specially true just preceding a strike (e.g., the FORRESTAL) when it is required that a very high concentration of munitions and flammable fuel be on the flight deck, and munitions for the follow-up strike are already being rolled out onto the hangar deck. Attack by the enemy at this particular moment would be the most propitious from his standpoint. Under nuclear or BW attack, when a ship will have to be buttoned up (as proposed in the STOPS program), special fire problems will be created because of the radical changes in ventilation and temperature. In the engine and boiler rooms of a conventionally-fired ship, temperatures exceeding the flash point of Navy Special Fuel Oil are likely to be reached; and spillage of fuel for any reason would thus pose an explosion hazard in a very vulnerable part of the ship.

Equipment

18. Many kinds of special equipment aboard Navy ships may contribute to or become fire problems. Galley fires have been numerous as the result of spontaneous ignition of fats. Compressors have caused fires and explosions as the result of ignition from lubricating oil deposits, and the like, at high pressures. The liquid oxygen plant on board ships is a special hazard because of the fact that fires burn more rapidly and intensely in an enriched oxygen atmosphere (4). Electrical motors, welding gear, electronic high frequency gear (1), and similar equipment may be spark ignition sources in any flammable atmosphere. Ventilating systems may pose special problems since they may assist in spreading a fire by transfer of burning gases and because they may accumulate oily surface films which can be ignited and initiate or spread a fire. Water stills, steam pipes, laundry equipment, and the like provide hot surfaces which can ignite some flammable substances. Small portable gasoline and diesel engines, which are used for emergency power sources, are potential fire hazards. In general, however, most equipment fires are more readily confined and controlled than the fires caused by ignited jet fuels, AvGas, Navy Special, and similar petroleum fuels when present in such large quantities on ships.

Fire Prevention

Regulations

19. In general, naval instructions, procedures and training give good evidence that the Navy is extremely fire-prevention conscious (5,17,18). Almost everything to be done is required to be done in such a way as to

avoid unwanted fires. There are a multitude of fire prevention rules in the Naval Ships Technical Manual (17) covering the design, construction, and location of ship parts and equipment, for the storage and handling of hazardous materials, and for every imaginable operation. Noncombustible thermal insulation is used, fire resistant coatings are required, and flame arrestors are installed in ventilation systems. There are special precautions for the location and storage of gasoline, explosive gases, and similar flammables. There are limitations on quantities of stored combustibles, such as paper, records, files, office supplies, lubricating oils and greases, pyrotechnics, dangerous chemicals, and the like, and special places for their storage. But despite all of these or any additional regulations, fire prevention in the future will depend on whether or not the rules are followed, in other words, on the human element on board. If all the Naval Ships Technical Manual rules were kept up to date and followed, there would be fewer accidental fires indeed aboard our ships. Unfortunately, because of lack of special training, carelessness, ignorance and indifference, many fires do occur which should have been prevented.

Education

20. The Navy makes many attempts to educate its personnel by means of training courses, books, pamphlets, sign posters, and the like, too numerous to list here, in order to prevent fires. Because so many of the newer materials used aboard ship are highly flammable, these education and training procedures should be reviewed, condensed as much as possible, and brought up to date. As an example of such education, NAVAIR operates

a school at Bayonne, N. J., which gives instruction in safety in handling fuels (among other subjects) to those who will be responsible for handling fuels. However, there is a feeling among the technical staff at Command Headquarters that this school cannot be depended upon to be completely adequate for proper training, partly because of personnel assignment problems (i.e., not all of them attend the school), and because of the complexity and magnitude of the subject.

Specifications

- 21. Because of their high fire-disaster potential, petroleum fuels, lubricants, solvents, and related materials have special flammability requirements in their military specifications in order to keep down the fire risks in their storage, transportation, and use. Specifications for some of the more important petroleum products are shown in Table 1. It can be seen in the Table, that these combustibles must meet one or more flammability requirements in addition to their other specification requirements. The requirements for JP-5 jet fuel for a flash point temperature minimum of 140°F, and no more than 50% explosiveness, are of particular importance. It must be noted that there are no flammability requirements in the specifications for either AvGas or JP-4. As is well recognized, both of these fuels are extremely flammable due to high volatility; hence, no attempt has been made to set limitations on flammability per se.
- 22. Despite present Naval Ships Regulations, education and training techniques, and military specifications, fires (often of a disastrous

Table 1

⊢ ·	MPORTANT PET	ROLEUM AND REALT	IMPORTANT PETROLEUM AND RELATED PRODUCTS USED BY NA FLAMMABILITY REQUIREMENTS IN SPECIFICATIONS	USED BY NAVY WITH	TH
Material	Flash Point Minimum	Fire Point, Minimum	Autoignition Temp., Minimum	Explosiveness Maximum*	
	(oF)	(9F)	(0)	(%, at 125°F)	(at IAUVF)
Fuel					
Jet, JP-5	140			50	
Diesel (Marine)	140	6		Z,	
Burner Oil		200		3	
Ballistic	140		-		
Wissile (Ships)					
Rocket, RP-1	110	٠			
Lubricating Oil					
Aircraft (Piston)	420,470				
Turboprop				-	
General Purpose					
Hydraulic			•	·	
Mineral, Cylinder	- 49				
Steam Turbine	320			•	
Hydraulic Fluid					
Fire Resistant			1		Ċ
Power Transmis-	220	235	1050		1:04
sion			-		, OA
Catapult					1.00
Petrol. Base, Air-	500				
grain, ord.	· · · · · · · · · · · · · · · · · · ·				
Petrol. Base, rir	225		-		
CONTROL					

* "Explosiveness" is a measure of potential flammability hazard. It is the ratio (in percent) of the actual concentration of vapor in a closed space above a liquid (measured with an explosion meter) to the concentration at the lower flammability limit.

rapid compression (measured in a motored diesel-type engine under specified conditions) ** "Compression Ignition" is the compression ratio needed to cause incipient ignition by

magnitude) have occurred on naval vessels with alarming frequency.

This makes it all the more important to make equipment and materials as foolproof as possible and also to insist on control of dangerous properties to the maximum extent possible. Development and use of proper specifications and instructions are two important approaches, and in our opinion, the Navy's laboratories can be of considerable importance in developing not only reliable criteria for better product control and better test methods, but also in advancing our understanding and knowledge about flammability and its assessment.

Test methods can easily be misleading, even those developed by a large and supposedly knowledgeable industry. A case in point can be cited. The Navy uses a common commercial adhesive for mounting thermal and sound insulation onto bulkheads, etc., which is formulated with a petroleum solvent. The specification calls for a flash point in excess of 120°F, measured by the Cleveland open cup method. This adhesive was tested by the specification method and found to have a flash point of 145°F. However, when a sample of the same adhesive was placed in a closed container, it was found to be flammable at temperatures below 70°F. This result is caused by the accumulation of vapors which otherwise escape in the open cup tester. Use of such an adhesive in a closed (or poorly ventilated) space is hazardous because the men liberally daub large surfaces with it and, having a false sense of security, do not take proper precautions. Obviously, in this situation the specification is at fault, and a more meaningful test procedure should be used. The specification should insure that the accumulation of toxic and/or flammable levels of solvent vapors will not occur in use of such adhesives. Also, instructions requiring greater care in applying the adhesive are needed. Other such defects have also been noted, and also brought to the attention of those responsible for specifications. More similar action is needed on other products and practices.

Substitution of Less Flammable Fuels

Elimination of AvGas

24. Current short-range plans call for the elimination of AvGas from the FORRESTAL (CVA 59) and subsequent CVA aircraft carriers, and from the MIDWAY (CVB-41) in the near future (19). However, it is believed that AvGas will probably not be removed from the ASW aircraft carriers until 1975, at the earliest. This will eliminate the one highly volatile fuel from among the three basic fuels now on aircraft carriers and thereby reduce the fire hazards. It will also reduce the logistics problem. The fire hazard in tankers will also be reduced, particularly during fuel transfer operations at sea, since tankers would no longer have to carry AvGas. The transition to all jet aircraft (including helicopters) using the high flash JP-5 should definitely enhance safety. This was an important consideration on which the present plan is based.

Gelled Fuels

25. Special attention must be given here to "gelled" fuels because of the great amount of publicity they have been receiving during the past year or two (including in the popular press). These are conventional petroleum fuels which are thickened or gelled so that they will

not run when spilled. In other words, they will not come gushing out of an airplane tank if it is ruptured and will behave more like a solid when on fire than a liquid. Two processes of gelling have been the subjects of a moderate amount of research. The first process, historically, is to thicken the fuel with a soluble or dispersible solid additive (usually several percent) to produce a product somewhat like Napalm in appearance. Most such formulations are thixotropic materials. The second type of gelled fuel, which is receiving more attention today, is an emulsion of fuel-in-water (i.e., the water is the continuous phase) containing only about % or less water and a large amount of a surface-active agent (such as Span 80). More recently, formamide has been substituted for the water. Such an emulsion has an appearance like soft mayonnaise. Both types can be pumped, albeit it must be done carefully so as not to destroy the emulsion "structure," or the gel or emulsion will revert back to a fluid.

- 26. The more enthusiastic proponents of this scheme for promoting fire safety suggest that the gelled fuels could be prepared at the refinery. Today, this is unrealistic. At best they would have to be prepared by special "homogenizers" as close to the time of fueling aircraft as possible, because otherwise they would pose too many other handling problems resulting from accumulation of dirt, rust and water with accompanying serious complications.
- 27. It must be emphasized that gelled fuels, as presently formulated, are not ready for naval use today. There are still too many

problems that must be overcome. The solids used in thickened fuels are objectionable because of the residues left in aircraft fuel handling systems as the fuel evaporates. The processes for preparation of either type, emulsion or gel, still have a tinge of "black magic" in them if they are to yield a good product. If the equipment or procedure is a little faulty, a poor product results. On an aircraft carrier, gelling would have to be done before putting fuel into the service tanks because it is a relatively slow process. Very special nonshearing pumps would be needed to transfer them to the aircraft, and it is difficult to prevent shear when high velocities of pumping are required, as they now are.

- 28. A greater drawback is that present engines cannot "digest," nor airframes handle, today's gelled fuels. Considerable modification of engines and airframes would be necessary to accommodate them. This is because (a) the inside of the wing, with all its complex internal structure, is the fuel tank, and flow characteristics do not permit getting gelled fuel to the engine with present equipment, (b) the fuel itself is the working <u>fluid</u> in the present servo mechanism which feeds fuel to the engine, and (c) atomization of the fuel in the burners is viscosity-dependent.
- 29. The promise offered by gelled fuels in preventing a major disaster (caused by massive spillages of fuel on fire) makes them candidates for further research, but one must keep in mind the added complications in handling and use so that loss of life does not occur

from other malfunctions. There would be a greater safety advantage in gelled JP-4 (a wide-cut gasoline and, hence, highly flammable) than in gelled JP-5 (a high-flash-point kerosene). Hence, present research by Army, Air Force, FAA, and industry is largely aimed at JP-4, but what is learned would be transferrable to JP-5. To our knowledge, Navy is not engaged in research on gelled fuel at the present time, but is following developments in the field closely.

Navy Fire Research

30. In-house fire research (ignoring fire extinguishment research which is covered in Section VI in this report) is relatively limited. The number and variety of projects is small, and they are being conducted in only a few Navy laboratories. Based on information supplied by the National Academy of Sciences--National Research Council in its 1965

Directory of Fire Research in the United States (20), and filling in a few known voids in the directory where possible with information from other sources (such as NARDIS and DNL), the following is a brief listing of the fire research programs conducted by naval laboratories and pertinent to this Section of the report.

(a) Naval Aeronautical Engine Laboratory

(1) Investigation of Flammability Conditions within Aircraft Fuel Tanks (FAA sponsored)

(b) Naval Air Turbine Test Station

(1) Full Scale Power Plant Turbofan Installation Fire Tests (FAA sponsored)

(c) Naval Applied Science Laboratory

- (1) Effect of Extreme Thermal Environment on Advance Design of Naval Vessels
 - (2) Development of Water-Base Fire Resistant Hydraulic Fluids

(d) Naval Civil Engineering Laboratory

(1) Protective Construction against Thermal Radiation

(e) Naval Radiological Defense Laboratory

- (1) Computer Program for Evaluating Incendiary Hazards of Nuclear Attack (OCD sponsored)
- (2) Ignition and Response of Materials to Intense Thermal Loading (DASA sponsored)

(f) Naval Research Laboratory

- (1) Study of the Interrelationships of Physicochemical and Flammability Properties of Liquid Hydrocarbons and Their Mixtures
- (2) Study of the Ignition and Burning Characteristics of Materials in Unusual Atmospheres, e.g., Variable Oxygen, Pressure, Diluents
- (3) Study of the Generation and Discharge of Static Electricity in Hydrocarbons

Other Government Research (20)

31. Significant fire research projects on liquid and gaseous flammables and their ignition are also being performed at other Government laboratories and elsewhere which is of value to and is (or can be) used by the Navy. Some examples of pertinent in-house fire research programs (excluding fire extinguishment research) of other Government laboratories are as follows:

(a) Federal Aviation Agency

- (1) Preliminary Crash Fire Studies of Ignitibility and Combustibility of Gelled Fuels
 - (2) Sparking Hazards of Structural Materials (Crash Landings)

(b) Bureau of Mines

- (1) Autoignition Temperatures of a New Engine Lubricant at Reduced and Elevated Pressures (sponsored by Monsanto Chemical Co., St. Louis, Mo.)
- (2) Ignition Characteristics of Fuels and Lubricants (sponsored by USAF)
 - (3) Flammability of Propellant Combinations (sponsored by NASA)
 - (4) Hydrogen Safety (sponsored by NASA)
 - (5) Studies of Air Flows into Uncontrolled Fires (sponsored by NBS)
 - (6) Flammability of Halogenated Hydrocarbons
 - (7) Hybrid Flame Studies
- (8) Investigation of Flame Propagation Characteristics in Layered Gas Mixtures

(c) National Bureau of Standards

- (1) Mechanism of Flame Spread (sponsored by OCD)
- (2) Growths of Fires in Model Enclosures
- (3) Improved Smoke Measurement Methods
- (4) Influence of Chemical Additives on Flame Combustion Speed

(d) <u>U.S. Air Force</u>

- (1) Hazardous Vapor Detection
- (2) Materials Fire and Explosion Hazard Characterization
- (3) Portable Hydrogen Fire Detector
- (4) Information Analysis of Fiber Optics Bundles for Hazard Detection

Recommendations

General

- 32. Of the many flammable materials on board Navy vessels, petroleum fuels, because they are designed to be burned, and because they are carried in such large quantities, pose a particularly large potential for disaster, especially on aircraft carriers and tankers. However, the Navy has been well aware of these hazards and has already taken many steps by both choice of fuels (by specifications) and by handling procedures and instructions, to minimize the danger. Radical changes in fuel properties to make them less flammable might easily impair their usefulness, performance, and availability, or might create other hazards (i.e., toxicity, equipment malfunctions, etc.). The greatest safety threats of fuels and other petroleum products are in their misuse or mishandling through carelessness, ignorance, faulty or poorly designed equipment, improper maintenance, and so forth. Constraints imposed by operational requirements also enhance the fire hazard, especially on aircraft carriers preparing for a strike.
- 33. Much is already known about the flammability properties of fuels, and this information has been widely disseminated by manuals, instructions, etc. Cognizance of the hazards has been taken in the design of fuel-handling systems and in their specifications. Nevertheless, more needs to be done in both the research sense and in the interpretation (or translation) of such knowledge to make it available and useful to the Navy's designers, operators, and crew. Although fuels have probably been studied more extensively than other combustibles, a body of new knowledge

about the latter also exists which can be applied by the Navy. Interestingly enough, much of this is of the "common sense" variety, which, unfortunately, is not always so "common."

34. Short-Term Recommendations

- (a) Enhance fire hazard and toxicity awareness among present and future operators by: greater insistence on safety instructions and education; closer attention to following Navy manuals and regulations; more intensive instruction of midshipmen at the Naval Academy; and more training through greater use of actual demonstrations and other visual aids.
- (b) Insist on better housekeeping and practices to avoid: spillage; leakage; accumulations of combustibles (especially during construction); unnecessary potential ignition sources near combustibles (h.f. radar, static, welding, open flames, sparks, photoflashes, hot surfaces, etc.); conflicting operations (e.g., hot or electric work during fueling or defueling); and malfunctions of equipment (by frequent servicing and maintenance).
- (c) Insist on maintaining a minimum flash point for JP-5 of 140°F. There is industrial pressure to lower this minimum value in order to increase fuel availability. NRL is investigating the flammability of JP-5 and other petroleum fuels (13-16).
 - (d) Abet the present plan to remove AvGas from aircraft carriers.

35. Intermediate-Term Recommendations.

(a) Develop and install better detectors and alarms for smoke and fire, and for the accumulation of hazardous concentrations of flammable or toxic vapors.

- (b) Develop a more meaningful "explosiveness" test for JP-5,
 Navy Special, and other high flash fuels. (The present specification
 test has decided defects in it. NRL is already deeply involved in
 this problem.)
- (c) Develop more foolproof devices to prevent spillage during fueling of both ships and aircraft.
- (d) Make a systems study of spacings and geometrical arrangements of aircraft on the flight deck of carriers, especially just prior to a strike, to determine whether greater safety from hot starts and chain reactions can be achieved within the constraints of operational requirements.
- (e) Develop improved techniques for crew instruction, education, drills, and practices in fire safety.
- (f) Review the present specifications and test procedures (related to flammability) for combustibles being used in quantity (including adhesives, solvents, etc.) to determine whether more meaningful controls and procedures could be applied.

36. Long-Term Recommendations.

- (a) Perform research on spurious forms of ignition of hydrocarbon fuels such as static, electromagnetic fields and spontaneous ignition.

 (NRL has an active investigation in progress on static.)
- (b) Study means for preventing the hazard associated with spontaneous ignition due to ram heating in supersonic flight.
- (c) Continue research at NRL on flammability properties and principles of hydrocarbon fuels to develop background knowledge on which to establish safer fuels and handling and usage practices.

- (d) Continue NRL study of specifications and their test procedures for fuels and other commonly used flammables with the view of developing new or more meaningful flammability controls for hazards associated with ullage (an almost empty tank full of flammable vapors is a greater explosive hazard than a tank full of liquid), explosivity, spontaneous ignition, compression ignition, shock ignition, etc.
- (e) Continue evaluation of gelled fuels for fire minimization, commensurate with the effects of their unusual properties on other important criteria of usage, handling and safety.

References

- 1. Woods, F. J., Williams, K. G., and Carhart, H. W., "Shipboard Studies of Fuel-Vapor Ignition by Radio-Frequency Arcs," NRL Report 5443, Jan. 25, 1960.
- 2. Leonard, J. T. and Carhart, H. W., "Electrical Discharges from Fuel Surfaces," Second Conference on Static Electrification, London, England, 8-10 May 1967.
- 3. Liebman, I., Spolan, I., Kuchta, J. M., and Zabetakis, M. G., "Ignition of Tank Atmospheres During Fuel Loading," Preprint No. 36-65, 30th Midyear Meeting of the American Petroleum Institute's Division of Refining, Montreal, May 11, 1965.
- 4. Woods, F. J. and Johnson, J. E., "Flammability in Unusual Atmospheres. Part 2. Selected Materials in Oxygen-Nitrogen and Oxygen-Helium Mixtures at Pressures up to 315 PSIA," NRL Report 6606, 22 May 1967.
- 5. Fundamentals of Petroleum, Bureau of Naval Personnel, NAVPERS 10883-A, Revised 1965.
- 6. Sax, N. I., "Dangerous Properties of Industrial Materials," Second Edition, Reinhold, New York, 1963.
- 7. "Threshold Limit Values for 1966," 28th Annual Meeting of the American Conference of Governmental Industrial Hygienists, Pittsburgh, 16-17 May 1966.

- 8. Brophy, J. E., FitzSimmons, V. G., O'Rear, J. G., Price, T. R., and Zisman, W. A., "Aqueous Nonflammable Hydraulic Fluids," Ind. Eng. Chem. 43, 884 (1951).
- 9. Sullivan, M. V., Wolfe, J. F., and Zisman, W. A., "Flammability of the Higher Boiling Liquids and Their Mists," Ind. Eng. Chem. 39, 1607 (1947).
- 10. Bried, E. M., Kidder, H. F., Murphy, C. M., and Zisman, W. A., "Synthetic Lubricant Fluids from Branched-Chain Diesters--Physical and Chemical Properties of Pure Diesters," Ind. Eng. Chem. 39, 484 (1947).
- 11. Atkins, D. C., Jr., Baker, H. R., Murphy, C. M., and Zisman, W. A., "Synthetic Lubricant Fluids from Branched-Chain Diesters--Development of Additives and Lubricating Oil Compositions," Ind. Eng. Chem. 39, 491 (1947).
- 12. Cohen, G., Murphy, C. M., O'Rear, J. G., Ravner, H., and Zisman, W. A., "Aliphatic Esters. Properties and Lubricant Applications," Ind. Eng. Chem. 45, 1766 (1953).
- 13. Affens, W. A., "Flammability Properties of Hydrocarbon Fuels. Interrelations of Flammability Properties of n-Alkanes in Air," J. Chem. Engr. Data 11, 197 (1966) (c.f. NRL Report 6270).
- 14. Affens, W. A., "Flammability Properties of Hydrocarbon Fuels.
 Part 2. The Importance of Volatile Components at Low Concentration
 on the Flammability of Liquid Fuels," NRL Report 6578, 10 July 1967.
- 15. Affens, W. A., "Flammability Properties of Hydrocarbon Solutions in Air," Preprints, General Papers, Petroleum Division, American Chemical Society, <u>12</u>, 35 (1967).
- 16. Affens, W. A. and Carhart, H. W., "The Effect of Ullage on the Flash Point and Lower Flammability Limit Temperatures of JP-5 Jet Fuels," NRL Memorandum Report 1735, November 1966.
- 17. Naval Ships Technical Manual, NAVSHIPS 250-000.
- 18. Principles of Naval Engineering, Bureau of Naval Personnel, NAVPERS 10788, 1963.
- 19. CNO Message to Chief of Naval Material, No. 291258Z, June 1967.
- 20. <u>Directory of Fire Research in the United States</u>, National Academy of Sciences-National Research Council, 3rd revised edition, 1965.

Section III. Hazards Arising from Fires on Shipboard from Organic Materials Such as Paints, Plastics, and Insulation Materials

by Dr. A. L. Alexander and Mr. J. E. Cowling Naval Research Laboratory Washington, D.C.

Introduction

1. Since another section on the subject of fire hazards (1) discusses in detail the tolerable limits of noxious gases in enclosed environments, these will not be repeated here. However, an effort is made to indicate the extent to which organic materials contribute to and aggravate this situation. These include paints, plastics, organic thermal and electrical insulation materials, deck coverings, furnishings, as well as supplies and stores of organic origin.

Present Painting Practices

2. Since organic coatings are used extensively throughout most ships, this discussion will be directed first to the use of paints and especially to their misuse. Work has been done to eliminate hazards resulting from the tendency of paints to promote combustion and to contribute to the toxicity of atmospheres in confined spaces. NAVSHIPS Technical Manual (2) contains complete and detailed instructions for painting ships from masts to the keels. This Manual has undergone frequent revision as new and improved materials and practices have become available. Hazards from paint would be greatly decreased, if assurance could be obtained that materials and procedures outlined therein would be closely followed. This Manual recommends that painting be done no more often than is considered necessary for adequate preser-

vation. It is recognized, however, that painting to improve ship appearance must be tolerated. It is stipulated further, where the existing paint on bulkheads with that to be added with repainting exceeds a total average thickness of 5 mils (0.005"), that all old paint be removed by scraping before repainting begins. It was demonstrated by the Industrial Test Laboratory at the Philadelphia Naval Shipyard (3) that thin paint films rarely propagate combustion. Furthermore, if the paint is decomposed by heat, it is obvious that the thinner the film the less will be the amount of noxious material delivered into the ship's atmosphere. It is believed that the regulations relating to old paint removal sometimes give way to expediency or to extenuating circumstances. For example, it has been reported by personnel of the Naval Ship Engineering Center (Code 6101) that during a recent overhaul of the USS MIDWAY, the cost of removing the thick existing paint was considered to be excessive, or at least that insufficient funds were available. As a result none of the old paint was removed, and the repainting simply added to the bulk of the coating already on all interior surfaces.

3. In this connection it should be emphasized that even a so-called "fire-retardant paint" loses much of its fire retardancy in proportion to thickness of the accumulated paint film. Reference (2) lists a recommended thickness for the application of every approved coating material, and these range from 0.5 mil for the initial coat of metal conditioner to 3.5 mils for some of the heavier enamels of high solids content. Standard practice for painting the metal

surfaces of interior compartments requires one coat of a metal conditioner, the organic portion of which is polyvinylbutyral resin, followed by two finish coats of chlorinated alkyd (fire-retardant) paint on all bulkheads and ceilings. The basic structure for the chlorinated alkyd resin is as follows:

C1
$$C1 - C - CH_2CH - CH_2O - C - (CH_2)_{16}^{CH_3}$$
C1 $C1 - C - CH_2CH - CH_2O - C - (CH_2)_{16}^{CH_3}$

This formula is listed for purposes of identifying a possible source of hydrochloric acid, chlorine, or phosgene, which will be discussed subsequently. Living quarters, messing facilities, recreation spaces, and connecting passageways also receive this same paint system. Similarly, specific recommendations are available for painting ship exterior surfaces. These surfaces, especially those exterior areas above the boot topping where free access to the atmosphere is readily available, are not considered too pertinent to this report. Paints on interior walls on hangar deck bulkheads should be considered as contributing to possible fire hazards and are included in the following discussion.

Plastics and Thermal Insulation Materials Aboard Ship

4. Fiber glass insulation (4) is used almost exclusively on surface ships. This material should not cause fire problems. Polyurethane foam has practically eliminated corkboard in refrigeration systems.

In submarines some proprietary insulation materials are used of which

"Ensolite" (5) is typical. While the exact composition of this material is unknown, it contains substantial quantities of polyvinyl chloride. Detectable toxic conditions have occurred in submarines with the use of Ensolite which were traceable to the chlorinated solvents in the adhesive by which it is applied. This practice has been eliminated in submarines. However, the polyvinyl chloride in the Ensolite could serve as a source of chlorine or hydrochloric acid during burning or thermal decomposition. If similar materials are used on surface ships, they will also present fire and toxic hazards.

Electrical Insulation Materials

while under construction in December 1960 at the New York Naval Shipyard, there was strong evidence that the flames had been propagated through many compartments of the ship along the ship's electrical cable wire-ways. There was particular concern that groups of cables (especially when insulated with polyethylene) could propagate flame through collars in non-watertight bulkheads. The Materials Laboratory, New York Naval Shipyard, investigated this possibility, and their findings (6) demonstrated, in fact, that fires could be propagated through non-watertight bulkheads by polyethylene-insulated electrical cable. This work showed further that propagation of fire through bulkheads could be arrested by "stuffing boxes" containing a mineral-type filler made by the Johns-Manville Corporation and referred to in reference (6) simply as "Code A Compound." The damage caused aboard the CONSTELLATION was among the most severe ever sustained by a major ship during construction. The extent to which losses in

electronic equipment were sustained is described by Shor and Milano (7). Much of this loss was attributed to the electrical cabling in the fire-affected area. This cable with polyethylene insulation was suspected of feeding the fire, and its decomposition products contributed materially to the composite damage.

- 6. Discussions with Mr. Frank Richardson (Code 6157E) NAVSHIPENGCTR revealed that all known organic insulation material for electrical wire and cable will propagate fire through bulkheads unless there exists positive means to arrest the flame. To arrest fire, stuffing boxes are now required, as described in reference (6), wherever electrical cable passes through non-watertight bulkheads, and these are considered effective in arresting flame propagation by this route. Almost all types of electrical insulation can be found aboard ship. However, where possible, the more flame-retardant types, such as nylon, are used.
- 7. Various tests conducted under the auspices of NAVSHIPENGCTR (Code 6157E) have revealed other interesting facts concerning the flammability of plastics. Among these are the following:
- (a) Fiber glass-filled plastics, such as nylon, will burn much more readily than unfilled pure nylon material. (NRL's observations on filled and unfilled coatings support this conclusion.)
 - (b) Even an organic compound considered to be self-extinguishing will propagate flame if, while exposed to heat, it melts and is wicked into a material such as the wire armour used on most ship cables.
 - (c) Presently NAVSHIPENGCTR (Code 6157E) is concerned with the possibility of fire propagation through fully enclosed metal channels

and troughs which are widely used in ship construction. It is not known, for example, whether these enclosed areas would tend to extinguish and/ or confine the fire in the trough-ways, or, on the other hand, might act as chimneys or flues which would hasten the spread of the fire.

- (d) Fluorescent lighting is widely used aboard ship, and the lenses of these fixtures usually consist of acrylic plastic which will burn. The possibility of replacing these lenses with polycarbonate is presently under investigation. While this material is not self-extinguishing, it burns with a dull-yellow, low-heat flame and produces no known toxic degradation products other than those of normal combustion.
- (e) A major problem is the provision of emergency lighting for smoke-filled corridors and compartments aboard ship. Presently there is no satisfactory solution of this problem. The need for such lighting, of course, is two-fold: (a) to aid in the evacuation of personnel from these spaces and (b) to assist damage control parties in their movement about the ship to extinguish the fires.

Deck Coverings

8. Innumerable types of deck covering are used on surface ships. These include deck tile (composed largely of polyvinyl chloride), slip-resistant coverings, rubber terrazzo, rugs and pads, vinyl foam surfaced with vinyl sheet, and rubber mastic. The deck tile is a fire-retardant vinyl asbestos (8). This material, which contains only 10% polyvinyl chloride, is extensively applied to the interior metal surfaces of most surface ships. The rubber mastics approved are all proprietary materials with unidentified compositions. No data are available on their fire-

retardant or toxic qualities. Rugs are normally 100% wool, since no synthetics have been approved for shipboard use. While wool rugs have a tendency to burn, nylon or orlon will melt and decompose in contact with extreme heat or flame.

Toxicity Hazards Associated with the Above Materials

Paints

- 9. It is generally assumed that paints applied as described in reference (2) do not contribute appreciably to the ultimate size of a shipboard fire nor to the toxic gases associated with it. This assumes, of course, that only a relatively thin film is present which is normally self-extinguishing when the source of ignition is removed. The hazards associated with thick films of paint were discovered early in World War II, when thick paint accumulations in the ships lost or damaged at Pearl Harbor were shown to contribute to the extent of damage and casualties caused by fire and noxious fumes. This experience was responsible for the existing specifications limiting the accumulation of paint on bulkheads to 5 mils.
- 10. By limiting paint thickness, it becomes exceedingly difficult for a fire to spread between compartments as a result of the paint igniting on the reverse side of a bulkhead against which a fire is in progress. Similarly, the continuance of combustion along a corridor or passageway is unlikely from the burning of the paint film alone. In order to eliminate even these prospects, fire-retardant paints were developed by the Industrial Test Laboratory, Philadelphia Naval Shipyard (3),

retardant or toxic qualities. Rugs are normally 100% wool, since no synthetics have been approved for shipboard use. While wool rugs have a tendency to burn, nylon or orlon will melt and decompose in contact with extreme heat or flame.

Toxicity Hazards Associated with the Above Materials Paints

- 9. It is generally assumed that paints applied as described in reference (2) do not contribute appreciably to the ultimate size of a shipboard fire nor to the toxic gases associated with it. This assumes, of course, that only a relatively thin film is present which is normally self-extinguishing when the source of ignition is removed. It should be recalled that the hazards associated with thick films of paint were found early in World War II, where accumulations of thick films of paint in the ships lost or damaged at Pearl Harbor were shown to contribute to the extent of damage and toxicity by fire. This experience was responsible for the existing specifications limiting the accumulation of paint on bulkheads to 5 mils.
- 10. By limiting paint thickness, it becomes exceedingly difficult for a fire to spread between compartments as a result of the paint igniting on the reverse side of a bulkhead against which a fire is in progress. Similarly, the continuance of combustion along a corridor or passageway is unlikely from the burning of the paint film alone. In order to eliminate even these prospects, fire-retardant paints were developed by the Industrial Test Laboratory, Philadelphia Naval Shipyard (3),

and their use is recommended in reference (2) for all interior surfaces. Two techniques are commonly employed to render paints fire-retardant. One of these, and by far the most common, is to prepare them from a polymeric resin containing an appreciable amount of chemically-combined halogen, usually chlorine. The second technique is to employ pigments and additives, which when subjected to heat, intumesce to create a frothy noncombustible material. The latter, however, are relatively poor-quality paints and have not been considered seriously for shipboard use. 11. Deviations from recommended practices are known which may have contributed considerably to existing hazards, some of which were apparent on the USS FORRESTAL. In checking with the Chemical Laboratory, Norfolk Naval Shipyard, who inspected materials which went into refurbishing the FORRESTAL, it was learned that quality control on a large number of batches of fire-retardant paint had been so poor that large-scale rejections were made. As a result, during the FORRESTAL's refurbishing at Newport News, a shortage of fire-retardant paint occurred, and it is suspected that some nonchlorinated alkyd paints were substituted. It also was reported from the Chemical Laboratory that the fire-retardant paint was not quite equal in gloss and appearance to a nonfire-retardant paint. Instances have been observed where, in order to obtain these properties, the two paints have been mixed in equal proportions prior to application. By mixing the two formulations, appearance and working properties of the resulting material are improved, but fire retardancy is reduced as shown by studies at NRL and at other laboratories.

- 12. In addition to the chlorinated alkyds, which are the most widely used interior coatings, a number of other paints also contain chlorine and are in the fire-retardant category. These include some polyvinyl chloride, used for coating aluminum surfaces, and polyvinylidene chloride (Saran), which is used principally in coating the interiors of fuel tanks. In some instances materials are obtained from Qualified Products Lists when exact compositions are unknown.
- 13. Because they are organic compounds, all of these paints will burn when exposed to an intense fire or will decompose when subject to extreme heat. However, the fire-retardant materials are completely self-extinguishing, i.e., as soon as the source of ignition is removed, they will no longer continue to burn. Furthermore, the fire-retardant materials will not ignite ordinarily when heated from the reverse side of the bulkhead to which they are applied.
- 14. While some qualitative experiments have been made to determine the products of combustion and/or decomposition of these paints, little quantitative data are available. Some information has been developed on the decomposition of the polymers and resins used in these paints, but these processes have not been studied in the presence of such widely used pigments as zinc oxide, titanium oxide, antimony oxide, and certain coloring pigments. Early experiments at the Industrial Test Laboratory, Philadelphia Naval Shipyard, at the time the chlorinated alkyd enamels were first adopted, indicated that under intense heat the resulting decomposition released some hydrochloric acid. The products

of combustion, however, can be expected to be different from the products of thermal decomposition. Compounds derived from combustion can be expected to be those typical of the oxidation of organic materials, namely, water, carbon monoxide, carbon dioxide, and hydrochloric acid from the chlorinated resin. The products from thermal decomposition are potentially much more dangerous. These will include, in addition to those compounds immediately above, such toxic materials as vinyl chloride, vinylidene chloride, vinyl acetate, and possibly phosgene. However, the extent to which these compounds might be formed in a fire disaster is not known.

15. In order to obtain some estimate of the potential amount of toxic material that could derive from a typical ship compartment painted with a fire-retardant chlorinated alkyd paint, the following approximation can be made: In a compartment 10' x 20' x 8', there is an area of 680 sq. ft. of painted surface and 1600 cu. ft. of space. The surface required 42 lbs. of dry paint which is 6.5% chlorine or 2.73 lbs. This is equivalent to 1240 grams hydrochloric acid. While it is most unlikely that any considerable fraction of this amount might be converted during even a severe conflagration, only 7 milligrams per cubic meter or 5 parts per million are permissible as a threshold limit by the American Conference of Governmental Industrial Hygienists (9). Thus the potential exists for a severe situation should personnel be confined to such space for any considerable period.

- 16. While it was reported from the FORRESTAL that some hydrochloric acid was detected, it is thought that a more likely source might have been the electrolysis of seawater from the fire mains in the battery compartment.
- 17. Some carbon monoxide and carbon dioxide will result from the decomposition or burning of the paint, but it is believed that this will be quite small compared to the quantities produced in the main fire itself. The following is a calculation of the amount of carbon dioxide and carbon monoxide which might be derived from the combustion or decomposition of the paint in the same compartment cited above for the calculation of hydrochloric acid. Referring to the basic formula for the chlorinated resin, it requires 34 molecules of oxygen to oxidize each molecule of resin to carbon dioxide, water, and possibly hydrochloric acid. In order to determine the total quantity of oxygen required, let us assume the paint to be 5 mils thick from which it can be shown that 13.9 lbs. of resin are present on the interior surface. If z represents the total amount of oxygen required, then the following relationship should hold.

$$34 \times 32 = 720$$
 (720 = Molecular Weight of Resin) z 13.9

z = 20.8 lbs. of oxygen required.

Assuming the air in the compartment to be relatively dry at a pressure of 76 cm. of mercury and 25°C, it should contain 27.2 lbs. oxygen which theoretically is sufficient to consume all the paint. Since all the

oxygen could not be expected to be consumed evenly, and since additional combustibles are present, it is quite likely that appreciable amounts of carbon monoxide would result, in addition to the carbon dioxide. For continuous exposure in closed spaces, the carbon monoxide limit has been set at 25 parts per million.

18. In conclusion with reference to interior paints, a strict compliance with existing instructions and specifications would serve to reduce, if not completely eliminate, several of the hazards associated with paint.

Exterior Paint

19. On ship exteriors, alkyd and vinyl paints are used. Although the latter contain chlorine, the hazards associated with exterior paints, as pointed out in paragraph 3, are not considered too critical where products of decomposition or combustion can pass readily into the atmosphere except, say, during a major conflagration.

Other Shipboard Combustibles

- 20. Besides the highly flammable fuels, lubricants, munitions, pyrotechnic materials, and the like, which are found on board naval ships, there are large quantities of other combustibles which, although are not likely to cause a fire disaster, must also be given concern. These are plastic insulation materials and floor coverings, etc., and they will be divided for convenience as follows:
- (a) <u>Materials of Construction</u>--thermal and electrical insulation, wiring, etc.

- (b) <u>Furnishings</u>--furniture, upholstery, bedding (mattresses, pillows, blankets, sheets), rugs, mats, etc.
- (c) <u>Supplies and Stores</u>--clothing, fabrics, rope, paper, files, stationery supplies, plastics, paints, varnishes, solvents and thinners, foods (oils and fats, etc.), chemicals and drugs.
- 21. The relative hazard of combustibles will depend on many factors including not only flammability, but the type of ship, the manner and amount of handling, the nature of operations being performed, and the types of equipment being used which could ignite a fire.

Areas of Possible Investigation

- 22. Fire-retardant paints for military use can be divided into two types: (a) paints for noncombustible substrates such as metals and (b) paints for combustible substrates such as wood. The purpose of type (a) is to prevent spreading of a fire by a combustible paint film. Type (b) is used to protect the substrate by reducing its flammability or burning rate. In order to overcome the tendency for violations of prescribed painting practices aboard ship, such as the dilution of a fire-retardant material with a nonfire-retardant material, an approach is being made at NRL (10,11) to provide a paint system consisting of two coats of a completely retardant material followed by one coat of nonretardant material which provides all the good quality of a normal enamel and yet the system itself is fire-retardant.
- 23. One fact outstanding throughout this investigation of shipboard fire problems has been the general absence of sound, technically-based

information concerning the contribution of the wide range of materials found aboard ship. Insofar as can be determined, only the contribution of paints and electrical cable insulation to shipboard fires has been methodically investigated. Even here the investigation has been skimpy, because it has failed to identify qualitatively and quantitatively the components which were involved in the course of burning. There seems to have been no effort anywhere to make an overall evaluation of the shipboard fire problem and coordinate or correlate the bits of information spread diffusely through many offices and activities of the Navy Department. Even these scraps of information in some instances seem to be founded more on suppositions than on technical facts. In general, there is a dearth of documentation to support many of the alleged facts, with exception only in those areas pertaining to paints and electrical insulation.

Short-Term Recommendations

- 24. In order to insure against any recurrence of fires or toxics contributed by paints, it is recommended that the following be done:
- (a) Inspect all bulkheads and ceilings for determination of paint thickness. If this appears to be in excess of 5 mils, arrangements should be made to have the old paint removed prior to repainting.
- (b) Check existing paint for fire-retardant properties. This can be done by noting specification numbers of the paint at the most recent application or by quick analysis of the dry sample of scraped paint.
- (c) Check flammability of bedding, furniture, electrical and thermal insulation now in use.

Intermediate-Term Recommendations

25. Since evidence exists that toxic materials may be formed from decomposition of the existing fire-retardant paints, plastics, and other solid materials already discussed, it is recommended that appropriate laboratory work be instituted to determine quantitatively the composition and potential toxicity of the decomposition products evolved. Recently available infrared and rapid-scanning mass spectrometric methods used in conjunction with gas-liquid chromatographs make practicable the rapid chemical analysis of evolved gases and vapors from a wide variety of commercial or new products. With such data, it should be possible to determine the extent to which such fire-retardant materials may be used in closed spaces without producing unacceptable hazards. Assuming that such investigations reveal the presence of intolerable types and concentrations of decomposition products, reformulation of existing fire-retardant materials should be undertaken to eliminate such sources. This might be done, for example, by omitting a pigment combination, such as antimony oxide with halogen-containing materials which react when heated together in a matrix, such as in a paint film. Hopefully, a combination could be obtained whose decomposition products would be tolerable.

Long-Range Recommendations

26. Chlorine has been used largely in fire-retardant protective coatings because of its availability and the ease with which it can be substituted in the organic structures of many polymers. The literature suggests that bromine is considerably more effective in retarding fire,

and perhaps the preparation of bromine-containing polymers could produce materials requiring smaller amounts of halogen. However, the stability and toxicity of such materials would need review or investigation.

- 27. Many compounds of phosphorous display exceptional thermal stabilities and flame-retardant properties. In view of the existing situation, a re-examination of known polymer structures containing phosphorous might reveal potential materials which would be less toxic than those containing halogen.
- 28. Another promising approach is a search for catalytic additives to cellulosic materials which would have the effect of making that material flameproof. The addition of such a catalyst (Lewis acid or base) has the effect of dehydrating the basic molecule as temperature is raised with the formation of water and carbon. No volatile gases or other combustible materials are produced in such a reaction.
- 29. As a corollary to these approaches, a thorough investigation of the mechanisms of fire retardancy may point to new means of reducing combustibility in materials.

References

- 1. Ramskill, E. A., Section VIII, "Toxicity Aspects and Application of the Naval Protective Gas Mask to Shipboard Fires," of this report
- 2. Naval Ships Technical Manual, NAVSHIPS 250-000, Chapter 9190
- 3. Birnbaum, Leon S. and Markowitz, Morris, Ind. Eng. Chem. 40, 400 (1948)
- 4. MIL-I-742B, "Insulation Board, Thermal Fiber Glass," 21 May 1964

- 5. MIL-P-152800, "Plastic Foam, Unicellular, Sheet and Tubular Form, Elastomeric," 3 April 1962
- 6. Forbes, Robert J. and Behr, Samuel H., "Investigation of Flame Propagation of Electric Cables Through Bulkhead Penetrations," Materials Laboratory (Brooklyn Naval Shipyard) Report, Project No. 6322, 1 December 1961
- 7. Shor, S. W. W. and Milano, V. R., Bureau of Ships Journal <u>10</u>, #7, 2 (1961)
- 8. QL-Mil-T-18830A, "Tile, Plastic, Fire Retardant," 24 May 1963
- 9. Steere, Norman V., Journal of Chemical Education 44, #1, A-45 (1967)
- 10. Walton, T. R., "The Development of a Nontoxic Self-Extinguishing Paint for the Interior of Nuclear-Powered Submarines," NRL Report 6304, 5 August 1965
- 11. Walton, T. R., "The Influence of a Fire-Retardant Undercoat on the Burning Characteristics of a Combustible Topcoat," NRL Report 6548, 22 May 1967

Section IV. Shipboard Fire Hazards of Pyrotechnics and Explosives

by Dr. J. E. Ablard U.S. Naval Ordnance Laboratory White Oak, Silver Spring, Maryland

Fire Hazards with Pyrotechnics

- 1. There are three general classes of pyrotechnics to consider from the standpoint of their compositions.
 - (a) Jellied gasoline (Napalm)
 - (b) Compositions containing metals which replace hydrogen in water
 - (c) Thermites
- 2. In the jellied gasoline class, the pyrotechnic contains only fuel. Oxygen from the air is necessary for combustion as well as providing a heat source for ignition. The latter is usually supplied by a material such as phosphorous which spontaneously starts to burn when exposed to air. The complete munition also contains some method for propulsion, which may be an explosive or a gas-generating propellant. However, the propulsion device is nearly always so well buried within the bomb that there would be a considerable delay before it prematured in a fire.
- 3. The obvious procedure to minimize damage from a Napalm bomb exposed to a gasoline fire would be to fight the gasoline fire in the recommended way. No program, either short-range or long-range, has occurred to us to reduce the fire hazard from a Napalm bomb. However, some of the programs to reduce the hazard of fuze operation in a fire which are discussed below are applicable to Napalm munitions which may have such fuzes.

- 4. The class of pyrotechnics containing water-reactive metals may or may not also contain an oxidizing agent. This class includes flares, photoflash bombs and cartridges. The particular hazard in this class is that if a fire once starts, whether between the metal and air, or between the metal and its oxidizer, the water can contribute to the fire rather than smother it. It has been shown that large amounts of water can cool down a small magnesium fire to the extent that the flame is extinguished. However, the hazard still remains from hydrogen which continues to be evolved and which is extremely likely to explode. Furthermore, the ability to cool a magnesium flame with water is certainly dependent on the ratio of burning magnesium to water. It is unlikely that a large magnesium fire can be smothered with a reasonable amount of water. Considerable quantities of sand or graphite are the recommended blankets. These are not particularly available at sea. Since these items are stored in a locker separated from all other items, a quick jettisoning device might be feasible.
- 5. It was assumed in the preceding paragraph that the magnesium fire had already started. In several recent cases, flares have been ignited inadvertently as the result of premature fuze action. This Laboratory has recommended that pyrotechnic fuzing be revamped to provide environmental safety as is contained in explosive munitions.
- 6. The R and D programs to be recommended for this class of pyrotechnics are:
- (a) Replace current fuzing with types that require some force generated by the environment which is experienced only when the weapon has been deployed.

- (b) On a longer-term basis, attempt to replace magnesium in flares by some thermoluminescent material. Magnesium is both a heat generator and a light generator. All the other metals which even approach magnesium in this regard are also water-reactive. However, a cerium oxide gas mantle gets its heat from another chemical reaction. Thus one system is known in which the heat-producing material and the light-producing material are separated. Perhaps if attention could be drawn to this possibility, a flare could be developed which did not require magnesium. This suggestion has been considered before but not developed due to its apparent high cost.
- 7. The third class of pyrotechnics, labeled thermites, in addition to the aluminum iron oxide materials which traditionally bear this name, should include all the metal-oxides, metal-chromates, metal-perchlorates, metal-nitrates, etc. In these mixtures the metal components do not react exothermically with water to produce hydrogen. These are usually easily ignited, and considerable heat is produced per gram of mixture. They do not normally burn to a detonation. In munitions they are extremely useful because of these qualities, but they are very seldom required in quantities greater than a gram or so per munition. Therefore, they do not in themselves represent a fire hazard. On the other hand, their purpose is to set off propellants or explosive trains. The methods to be recommended for reducing the hazards due to these materials are therefore the same as those to be discussed below under explosives.

Fire Hazards from Explosives

- 8. It is convenient to separate explosives into three classes dependent on their uses in munitions: primary explosives, booster explosives and high explosives. The most important primary explosives used by the Navy today and for the foreseeable future in conventional weapons are lead styphnate and lead azide. Fortunately, they are very stable to heat; but in addition, they are only used in Navy munitions ahead of the safety and arming mechanisms. Hence by design, if a munition containing them is subjected to a fire, and even if they get hot enough to detonate, they will cause no further hazard since the detonation will be stopped at the safety and arming mechanism.
- 9. Booster explosives, on the other hand, are used to transmit the detonation from the safety and arming mechanism to the main charge. If they get hot enough to detonate, they are designed to set off the main charge. Many fuzes and boosters contain tetryl. Some contain a mixture known as CH-6 whose explosive component is cyclotrimethylene trinitramine (RDX). Atomic weapons contain pentaerythritol tetranitrate (PETN). Though RDX is somewhat more resistant to heat than tetryl or PETN, all of these explosives are less chemically stable than the high explosive (HE) load. Consequently, booster explosives may represent a severe hazard.
- 10. The main charge or high explosive charge is also susceptible to burning to a detonation. The conditions which lead from burning to detonation are not well understood. A continuing effort at this Laboratory

and elsewhere is addressed to this problem. The need for this effort was recognized when high energy propellants were observed to burn to a detonation in rocket motors. However, the key factors which control the deflagration to a detonation transition (DDT) process are still not known. It has been shown that for small diameter explosive charges and probably also for thin layers of explosives, the DDT process takes place more frequently and more certainly when the walls of the container are dense and thick, i.e., the explosive is under "high confinement." But there are enough cases on record to make it necessary to suspect that a large charge of explosive which has been heated in a fire for minutes is likely to detonate whether confined or not. Thus, all explosively loaded munitions, whether fuzed or not, when caught in a gasoline fire must be treated as likely to detonate.

11. The R and D program recommended for booster explosives and high explosives is based on the supposition that after a fire starts, fire-fighting equipment with profuse quantities of water will be immediately applied to the fire. These suggestions are therefore intended to delay the initiation of burning and/or delay the DDT process. They will not prevent burning nor reliably prevent detonation if the fire continues for more than a few minutes. Thus a concurrent program to provide automatic or semi-automatic fire extinguishing should be started.

These suggestions will provide the necessary few extra seconds required to get the semi-automatic fire-fighting equipment into full operation.

- 12. The above-mentioned program is as follows:
- (a) Full-scale tests with instrumentation should be run to determine the time to detonation of several munitions in a JP-5 fire. Some of the components should be dummy explosives in order to determine which components by their composition and their position in the warhead are most likely to detonate first. This program is now underway at the Naval Weapons Laboratory, Dahlgren, Virginia, for general-purpose bombs and the Mk 80 series bombs, but it should be extended to rockets, photoflash bombs and any externally carried pyrotechnic items with and without igniters and also to fire bombs.
- (b) Wherever performance criteria will permit it, thermallyresistant explosives should be substituted for those now in use. A
 specific case which would require little further research and development
 would be to replace tetryl and much of the CH-6 by hexanitrostilbene (HNS),
 a new thermally-stable explosive which has already been produced in
 reasonably large quantities and has been released for use in the F111B
 aircraft pilot's compartment ejection equipment.
- 13. The current list of thermally-resistant explosives does not contain any with high density and high energy equivalent to RDX. Thus, some applications would sacrifice enemy kill probability for safety in a fire if direct substitutions were to be made. On the other hand, it was found that diaminotrinitro benzene (DATB) used in a pressed plastic-bonded explosive permitted a high kill probability for the Sparrow III continuous rod warhead. There are other new explosives now known with greater thermal resistance than DATB. A study should be made of all

munitions to see which could gain from replacing their explosives with thermally resistant explosives without unacceptable loss in kill probability.

- 14. A longer-term R and D program should be started to provide insulation for the explosive components in one or more of the following ways:
- (a) Increase the thickness of the "cavity paint." While this would be simplest from the availability standpoint, it may be difficult to do, and it does not seem very reliable unless a method can be developed to check the coating thickness.
- (b) Develop a thermoplastic coating technique containing asbestos, silica, or other well-known insulating materials which are compatible with explosives, yet could be deposited in a reliably thick coat on all cavities to be loaded with explosives. The coating thickness necessary for a given delay time to detonation should be determined.
- (c) Plastic cases should be used wherever this will not interfere with the operation of the munition. Plastic booster cans, for instance, would seem to be an easy possibility which would not interfere with the booster effectiveness but would interrupt the path for heat conduction from the nose fuze to the booster explosive. Plastic liners inside of guided missile warheads might be possible and, if so, could insulate the warhead explosive.
- (d) Develop a fire-retardant paint to coat over the explosively loaded parts. This might be an intumescent or an ablating coating or even a simple insulator. In addition, the coating would have to be extremely tough to enable it to withstand the abrasion of rough handling.

- (e) The current practice is to have considerable quantities of explosive stores stacked on carrier decks in various places. While this does not seem to be a desirable practice, it apparently is a necessary condition. Hence, we suggest that a fire-resistant tarpaulin be located on the market (or developed) which could be simply thrown over such munitions when stored open on decks. It is proposed that the aircraft carriers investigate the magazine-to-airplane-launch sequence to determine how much of the time the munitions could be covered by tarpaulins without interfering unacceptably with the operations.
- (f) There are now almost as many ways of determining the relative "cook-off" times or temperatures as there are laboratories engaged in work on explosives. It is well known, however, that explosives follow the general heat conduction equation with an exothermic term depending on the chemical reaction rate constants. All of the separate methods should depend on the same thermal diffusivity, heat of reaction and reaction velocity constants. Computer programs already exist at several laboratories for computing these constants from temperaturetime data. Full-scale tests are being run at the Naval Weapons Laboratory. Dahlgren, Virginia, and probably will continue in the future. A study should be made of the several ways of making the tests--probably it should include application of the computing programs to correlate the small-scale tests with the actual full-scale tests. The outcome of the study would be a recommended laboratory procedure for testing the relative susceptibilities to ignition which, in turn, would provide the fundamental constants best able to reproduce the full-scale experience. The method of reporting the results would be an important aspect to consider.

- (g) A long-range synthesis program should be continued to search for thermally stable explosives with energies at least equivalent to RDX. A shorter-range program should be addressed to improvement in the method of making HNS and perhaps other useful thermally-resistant explosives now known.
- (h) The detonation transition (DDT) study should be continued with the hope of dealing more effectively with the question of confinement on rate of DDT. It may also lead to chemical means for delaying DDT.

Recommendations on Fire Hazards with Pyrotechnics

- 15. Short-range programs.
 - (a) Provide quick jettisoning equipment for these items.
 - (b) Revamp the fuzes to provide better safety in handling.
- 16. Long-range program.
- (a) Develop chemical light sources which do not contain metals that react rapidly with water.

Recommendations on Fire Hazards from Explosives

- 17. Short-range programs.
 - (a) Replace tetryl in boosters and fuzes with HNS.
- (b) Full-scale tests of munitions with instrumentation in JP-5 fuel fires.
 - (c) Increase the thickness of cavity paint as a thermal insulator.
 - (d) Use plastic cases to contain the explosive wherever possible.
 - (e) Use fire-resistant tarpaulins over munitions stored on deck.

18. Long-range programs.

- (a) Develop explosive compounds and mixtures which are thermally resistant but are more energetic than HNS, DATB, or those now available.
- (b) Develop a new cavity coating which can reliably have a given thickness and has better insulation properties.
 - (c) Develop a fire-retardant and abrasion-resistant paint.
- (d) Correlate various cook-off tests through use of the differential equations of heat flow with chemical reaction.
 - (e) Continue detonation transition (DDT) program.

Section V. Fire Hazards of Propellants, Explosives and Incendiaries on Shipboard

by Ad Hoc Committee*, Dr. A. S. Gordon, Coordinator Naval Weapons Center China Lake, California

Introduction

- 1. In addressing the problem of reducing hazards of propellants, explosives, and incendiaries in shipboard operations, the Naval Weapons Center Ad Hoc Committee endeavored to identify the areas of greatest hazard. Based on their background, short, intermediate, and long-term recommendations are made for the solution of this complex and difficult problem. The Committee wants to emphasize that major attention should be on the areas which are mentioned. The suggested solutions are to be regarded only as possible starting points for further investigations.
- 2. Based on recent tragic naval experiences, the Committee is aware that fuels and ordnance** both present hazards, and that the combination of the two can increase the total hazard very much more than the sum of the separate hazards. In a flame environment all ordnance items are extraordinarily dangerous, and usually bombs present the major hazard.

^{*} Committee membership given in Appendix

^{**} As used in this report, ordnance includes rockets, missiles, incendiaries and munitions.

Recommendations

Electrical Firing Circuits

- 3. Since a rocket before burnout is an excellent mobile igniter for fuel, the prevention of an electrical-igniter malfunction can be of paramount importance.
- 4. Until an intermediate solution can be effected, it is recommended as a short-term measure that electrical ordnance leads not be connected to the aircraft until the aircraft has a clear field of fire which it maintains until takeoff.
- 5. From discussions with personnel who have had recent service on aircraft, it appears that a passive, but safe, stray-voltage check which can sense both AC and DC on a high-and low-sensitivity scale is not now available. As an important short-term measure, it is recommended that an adequate supply of such improved meters having adequate reliability be made available to all personnel conducting stray-voltage checks.
- 6. It is recognized that newer aircraft which carry a very heavy load of various ordnance will seriously impede launching operations if present arming procedures are conducted immediately prior to launching. A short-term measure recommended is a modification of the present one-wire system. All the "hot" leads should go to a multi-pronged plug which would be connected to a mating plug on the aircraft only when the aircraft is on the catapult. Until that time a dummy shorting-plug

should be in position on the multi-prong ordnance plug. This would permit arming the individual weapons "back in the pack" prior to start of aircraft. However, special precautions should be taken to assure the plane becomes armed just before takeoff.

7. A long-term recommendation is that the electrical firing circuits should be redesigned and installed. One possible solution is the use of an insulated and shielded two-wire system. All switches should be double pole, in order to break and make both the ground and the hot side together. All grounds should be terminated at one common point, including the wire shield. Such a measure requires modification of all aircraft firing circuits and stored ordnance and, therefore, will need long-range planning and action by the Navy.

The Problem of Ordnance "Cook-Off"

- 8. As noted earlier, when a fuel fire occurs in the vicinity of an aircraft loaded for combat, the greatest danger is the detonation, or very fast burning, of bombs. All bombs should be tested under the most severe conditions of exposure to flame with detonator and booster in place. Enough tests should be performed to give the results statistical reliability. A minimum "cook" time before explosion should be established before accepting the ordnance for shipboard use. This approach is an intermediate-term recommendation.
- 9. Intumescent and heat-radiation-reflective paints which are available at this time should be tested on ordnance in order to increase the flame

exposure time before violent reaction. For intermediate-term action it is recommended that the technology of coatings which are used to protect re-entry vehicles and propellant motor nozzles should be explored for their application to the above problem.

- 10. NOL, White Oak, Maryland and NWC, China Lake, California have developed high-temperature-resistant explosive compositions. Work in this area should be funded on a continuing basis as long-range research in order to develop explosives which will survive flame environments for even longer times than present compositions.
- 11. Since we believe an unconfined explosive is much less dangerous in a flame environment than a confined explosive, the possibility of developing a segmented case whose connections separate rapidly in a flame environment should be funded as a long-term investigation.

Faulty Wiring

12. Fires may also start in aircraft due to faulty wiring and spread via burning insulation. Since NASA has recently given considerable attention to this problem because of the Apollo disaster, it is recommended that NAVORDSYSCOM review a recent NASA report (1) in order to derive any possible benefit from advances in wiring stemming from recommendations made in that report.

Flares and Incendiaries

13. Flares and incendiaries present a unique, special hazard since they contain magnesium or other light metals which vigorously react

with water when they are in their burning configuration. Special techniques have been devised by NAVDAMCONTRACEN, Naval Base, Philadelphia, Pa., for fighting Mk-24 flares and magnesium fires (2). It is recommended as an early or intermediate-term measure that the above method be reviewed early and when adequately tested that the necessary fire-fighting equipment be supplied to the fleet; also it is recommended that personnel handling flares and incendiaries be trained in the special fire-fighting techniques.

Pop-Up Fire Nozzles

14. A viewing of the motion picture film taken of the FORRESTAL deck during the conflagration of July 1967 suggests that pop-up, high-volume, fire-fighting nozzles would have been very useful. It is recommended as an intermediate-term measure that these nozzles be adopted and that they be remotely controlled and capable of vertical as well as horizontal articulation. Such nozzles would have the further advantage of minimizing personnel exposure during a fire.

Camera Coverage

15. As aids to developing knowledge of how to improve safety, a short-term recommendation is made that unmanned and manned camera coverage of all operations involving ordnance handling and fueling of aircraft on a carrier be recorded on a continuing basis. The careful viewing of such film will uncover practices which may present severe safety hazards. The film will also be most useful to design engineers to guide their efforts to design equipment and ordnance to minimize hazards. We do

not recommend this film be used in order to obtain a basis for disciplining individuals but rather as a method of teaching how to improve present shipboard practices.

Preventive Maintenance of Shipboard Electrical Switches and Controls

16. Simple electrical limit switches on elevators and other switch

gear or controls break down during operation. Since sufficient

replacements are not on the Ships Spare Allowance List, switches are

by-passed pending the repair of the defective switches, thus intro
ducing safety hazards. A short-term recommendation is that these items

be included in sufficient quantity on the Ships Spare Allowance List.

As an intermediate-term recommendation, these switches and controls

should be redesigned to make them more reliable and impervious to

corrosion in the ship environment.

Safety Meetings

17. To supplement the Navy Training Program, a short-term recommendation is that regular, periodic, safety meetings be held aboard ship, especially Flight Deck Safety Meetings.

References

- 1. "Final Report of the Apollo 204 Review Board, with Appendices through G," (unclassified), April 9, 1967, Dr. Floyd L. Thompson, Chairman, NASA, Washington, D. C.
- 2. "Fire-Fighting Techniques Employed in Securing Fires Involving Mk-24 A.P. Flares," (unclassified) A/WMR; J.G.G., 9930, Ser 67, 14 February 1967. From CO, Naval Damage Control Training Center, Naval Base, Philadelphia, Pa. 19112, to CNO via Chief, Naval Personnel (Code PRSC 21)

Appendix

Ad Hoc Committee Membership

- A. Adicoff, Code 5059
- LT A. Dahlgren, Code 145
- J. D. DeSanto, Code 3006
- C. M. Drew, Code 5059
- L. M. Ellefson, Code 5507
- * A. S. Gordon, Code 5059
 - W. S. McEwan, Code 505
 - J. Sherman, Code 4542
- W. K. Smith, Code 40604
 - R. F. Vetter, Code 45711
 - W. C. Ward, Code 35601
- * Coordinator

Section VI. Shipboard Fire Fighting Methods,

Equipment and Materials

by Dr. R. L. Tuve and Mr. H. B. Peterson Naval Research Laboratory Washington, D.C.

Introduction

Because of the fire and explosion hazards associated with presentday aircraft operations, fire prevention and suppression problems are more serious and occur more frequently aboard aircraft carriers than any other type of naval vessel. Serious problems incident to the storing and high speed handling of large quantities of JP-5 jet fuel, pyrotechnic materials, explosives, rockets, incendiaries and ammunition, and automatic weapons, as well as the rapid launching and recovering of jet-engine-propelled aircraft, all combine to increase the possibilities of emergency fire or explosion situations during peacetime maneuvers or wartime operations of such ships. In previous sections of this report, the nature of the combustible and explosive materials and the sources of ignition on board naval surface vessels have been discussed, and various approaches for decreasing the associated hazards have been presented. It is the purpose of this Section of the report to review the present state of the art of fighting fires aboard such ships. Finally, recommendations on new and improved approaches for fire fighting methods, equipment and materials will be presented.

Equipment and Methods Presently Used on Aircraft Carriers

2. The flight and hangar decks of aircraft carriers are fitted with multiple air foam fire fighting systems which constitute the first line

of defense against fuel fires, the principal hazard in these areas. These independent systems are collectively called the High-Capacity Fog-Foam System which was originally developed by the Naval Research Laboratory in 1945-1949 (1-4). There has been little modernization or upgrading of these installations in the intervening 20 years (5-9).

3. The term "Fog-Foam" denotes the foam stream is a wide spray pattern of particulate droplets of foam as opposed to a long-range jet. The foam is formed by violent aspiration of air into high speed jets of water to which a foam stabilizing agent has been added. Foam stabilizers used are required to meet a Navy-developed specification (10) and are composed chiefly of partially hydrolyzed proteins derived from horn and hoof meal, feather meal, or soybeans. At the time of use the stabilizer concentrate is diluted by mixing with 15 parts of water. On aircraft carriers each fog-foam system consists of a 300gallon foam-concentrate storage tank, and a 1000 gal/min water capacity concentrate-injection station located on the second deck and is connected directly to the ship's fire main. Risers carry the resulting foam-making solution up to outlets on the hangar deck and the catwalk edging the flight deck. CVA's of the FORRESTAL class have 17 such systems throughout the length of the ship. Sectionalizing valves in the fire mains are used to segregate localized damage and permit independent operation. Emergency diesel-engine-driven pumps supply the fire mains in the event of loss of steam or electrical power.

- 4. All fire fighting on the flight deck is accomplished by dragging out hose lines from the catwalk in the event of an emergency. Both salt water and foam-making lines are provided. Actuation of the foam injection station and valves to the lines is accomplished by a push-button control on the catwalk adjacent to each outlet. The operation of laying out the hose is time consuming and is often made difficult by the presence of closely packed aircraft on the deck. The usual high wind conditions on the flight deck add greatly to the difficulty in attaining a proper fire-fighting position.
- 5. On the hangar deck hose lines are available from the foam system in addition to a fixed monitor nozzle which permits foam application to limited areas without the necessity of having a fire fighter at the nozzle itself. Actuation of the monitor and hose outlet is by means of a control at the station itself or from special protected "conflagration stations." Water-spray sprinkler systems are also installed overhead. In the newest carriers these systems are capable of spraying foam as well as water in accordance with principles established by the Naval Research Laboratory (11). The large hangar deck opening may be segregated by vertical water-curtains athwartships and with three fireproof sliding doors at times of emergency.
- 6. At the present time, 15-lb. carbon dioxide extinguishers are the only portable, first-aid, fire-fighting devices available on board naval surface vessels for quick on-the-spot use.

- 7. There are several types of water-fog and water-spray nozzles available for fighting fires when these fires occur in "ordinary" combustibles such as wood, paper, and rags. The "all-purpose" hand nozzle attached by means of a fire hose to the 100 psi. salt water fire main can be quickly adjusted to yield a long-range jet of water or a coneshaped spray. Another device for applying water is the low-velocity fog applicator which may be inserted into the all-purpose nozzle for forming dense screens of water particles in compartment fires or where gentle cooling and protection from flame are needed.
- 8. Compartments in which paints and flammable liquids are stored aboard aircraft carriers (and other surface vessels) are protected from fire by installed 50-lb. cylinders of carbon dioxide with which they can be flooded. These systems operate to inert the atmosphere within the compartment by displacing the air until the atmosphere is made up of 50 percent or more carbon dioxide. The system is actuated by pulling a release handle outside the compartment. Some systems also close ventilators and sound audible alarms to warn personnel to evacuate the space.
- 9. Protection against fire in machinery spaces is provided by hand-applicator nozzles connected to 50-lb. carbon dioxide cylinders and by portable foam nozzles and foam-injection equipment.
- 10. Magazines in which explosives and pyrotechnics are stored below the water line are protected from fire to some extent by high-rate water sprinklers or by flooding; hence, these compartments can be

deluged with cooling water. Ready magazines for rocket and pyrotechnic stowage on the hangar deck level are also provided with overhead water-sprinkling systems. However, as was found in the ORISKANY fire, these systems have insufficient capability to control a major conflagration.

ll. In addition, there are two other types of portable fire fighting equipment which deserve mention: (a) the gasoline-engine fire pumps and (b) the water-motor foam concentrate injection unit or proportioner. Item (a), the portable fire pumps, are employed when all other installed fire pumps may be disabled during an emergency. They are very light in weight, delicately adjusted mechanisms, and require a supply of motor gasoline. Item (b), the portable water-motor foam proportioner, is a device of close machine tolerances which employs the energy of the flow of water in a fire hose to inject foam-forming liquid concentrate into a water stream proportional to the flow demand. It was developed by NRL in 1940 (12).

Equipment and Methods Utilized on Other Surface Vessels

12. With the exception of the High-Capacity Fog-Foam System, all of the equipment just described is also employed in surface vessels of the Navy other than aircraft carriers.

Training Methods Employed for Shipboard Damage Control Personnel

13. If fires are to be combatted successfully aboard ship, much more consideration needs to be given to the educational methods which are being employed to train personnel and familiarize them with the various special devices and techniques necessary. Because of the extreme vari-

ability of fire emergency situations on aircraft carriers, as well as other surface vessels, automatic fire-fighting systems have been installed, but on a basis that does not afford total protection.

Education, training, preparedness, and the exercise of good judgment are still necessary to control and to extinguish efficiently the kinds of fires to be expected on ships.

14. In response to World War II combat needs, a number of Damage Control and Fire Fighting Training Centers were established at various naval stations during 1943-1944. An educational curriculum was set up at that time which included lectures in the elements of the chemistry of ignition and combustion and classroom demonstrations of the various kinds of fire fighting equipment aboard ship. The trainees were exposed to actual fire fighting "problems" inside a simulated ship's structure. There were also fire-extinguishing exercises by companies of trainees who manned lengths of fire hose while a "nozzle-man" directed foam or water fog on an open oil fire in a steel vessel or open pit. Much brute strength was demonstrated and soot-blackened skin resulted during these demonstrations, but the main wartime lessons taught were "Don't give up the ship" and "Conquer fear of fires and flames." With the exception of the addition of a simulated High-Capacity Fog-Foam Installation at the Naval Damage Control Training Center in Philadelphia, this curriculum has been basically unchanged from 1945 to date! Air personnel who handle flight and hangar deck fire fighting are trained in an Aviation Boatswain's school in Lakehurst, New Jersey.

"Light Water" and "Purple-K-Powder"

15. The development of "Light Water" foams by NRL in 1964 (13) has been a major advance in improving the effectiveness of fire-extinguishing This material is a blend of fluorinated surface-active compounds plus an ethylene oxide polymer for an adsorbed bubble stabilizer. When this foam is applied to a liquid fuel surface, a water-containing film is generated, through the process of foam decay, which floats and spreads spontaneously to cover the fuel surface with a film which prevents further release of fuel vapors. This behavior of water floating on the lower specific gravity fuel is due to the fluorochemical surfactant used and is the basis for the name "Light Water." NAVAIRSYSCOM has successfully been employing "Light Water" at Naval Air Stations since 1964. At these Stations "Light Water" has been teamed with a potassium bicarbonate-based dry chemical extinguishing agent (Purple-K-Powder or P-K-P) in a dual agent technique (14). The purpose of the dry chemical agent is to provide a heat shield for the fire fighters and to achieve the fastest possible "knock-down" of the fire. The "Light Water," applied simultaneously covers the fuel surface after the cloud of chemical has drifted away and prevents rekindling of the fire. Purple-K-Powder is also an NRL development (15). It is twice as efficient as the sodium bicarbonate materials previously employed for fighting fires.

Short-Term Recommendations

16. The High-Capacity Fog-Foam System on aircraft carriers has been outmoded by equipment design resulting from research progress during the past 20 years. Present complicated methods of operation of shipboard fire-fighting equipment have been widely shown to be unnecessary by

intervening developments since the original design in 1945. Therefore, the following recommendations are made:

- (a) Comparatively simple changes in valve controls and foamforming equipment can be recommended now and should be immediately
 planned to increase the speed of response and reliability of this system.
- (b) Methods of high-flow proportioning and storage of foam concentrate have been developed since 1945 by NRL in cooperation with industry; since they are simpler and less susceptible to failure than those now used aboard aircraft carriers, they should be adopted.
- (c) Because of the evidence that the fire-fighting systems are not adequately inspected and maintained by the ships' forces, a system for compulsory periodic test operation with foam of each fire-fighting unit should be adopted promptly. On-board observations by NRL representatives in 1%6-1%7 of the ORISKANY, RANDOLPH and INDEPENDENCE indicated inadequate inspection of these systems. The only available motion picture films of the FORRESTAL disaster showed the extremely slow response of the systems; whether that was due to mechanical or personnel failure could not be established.
- 17. The problem of obtaining more prompt response with sufficient fireextinguishing material to a fire in its early stage of development and
 spreading on the hangar or flight deck of a carrier has always been
 difficult and fraught with compromises. At the commencement of the
 FORRESTAL disaster, the initial JP-5 fuel fire on the flight deck
 appeared to cover only about 600 to 800 sq. ft. where it burned for
 approximately two minutes before the first explosion occurred. It is

believed that the prompt employment of the NRL "Twinned-Agent Unit" similar to the equipment used on Air Stations to attack this fire could have fully extinguished it within 20 or 30 seconds. A mobile unit of this type parked at the island with a trained and alert crew of one or two men could have reached the fire in about 6 to 10 seconds. Accordingly, the Twinned-Agent Unit was modified at NRL immediately after the FORRESTAL disaster from the configuration and vehicle now used at Naval Air Stations and in industry. Enclosure (A) illustrates the modification designed and recommended for use on carriers. On 15 August 1%7, demonstrations of the system were performed at NRL for VADM T. F. Connolly and on 17 August 1967, for ADM J. S. Russell. Promptly afterwards an emergency procurement of ten commercially-produced units similar to Enclosure (A) was ordered by classified TWX by the Chief of Naval Operations (16). Air shipment of these units, three to each carrier on "Yankee Station" in the China Sea, were to be completed by 20 September 1%7, less than six weeks after the FORRESTAL fire. An NRL technician will conduct a new training course at Naval Air Station, Cubi Point, Philippine Islands in the operation of the units for carrier-based fire fighters. A second-generation design of 70 additional "Shipboard Twin-Ball Fire Fighting Units" for fleetwide carrier installation has been authorized by telephone from CNO (OP-05), and design engineering of this model has been centralized at NRL and is underway.

18. The request has been made by CNO to NAVSHIPSYSCOM to equip the FORRESTAL flight deck with flush, deck-mounted, foam nozzles during her rebuilding period. It is strongly urged that these designs and

other systems of flight-deck fire protection be worked out by NRL personnel in consultation with NAVSHIPSYSCOM engineers.

- 19. Replacement of World War II, 15-lb. portable, carbon dioxide, first-aid extinguishers with the vastly more powerful potassium bicarbonate dry chemical (Purple-K-Powder) extinguisher with six-fold more efficient flame-quenching capacity per pound has recently been instituted by NAVSHIPSYSCOM (6154F) authorities. Purple-K-Powder is widely used by NAVAIRSYSCOM and industry. Fleet allowances of the new extinguishers should be completed as soon as possible.
- 20. After several serious and crippling fires had occurred in the machinery spaces of several ships, NRL (Code 6040) was requested by Ships Command (Code 6154F) in 1965 to conduct fire tests in the ship mock-ups at the Naval Damage Control Center in Philadelphia, using combinations of "Light Water" with Purple-K-Powder. It was determined that fires of the type occurring in these spaces could be extinguished in about one-fourth the time by the use of "Light Water" and Purple-K-Powder as compared with existing methods based on the application of water spray or carbon dioxide and air foam (17). Ship equipment designs to incorporate these results should be initiated by NAVSHIPSYSCOM.
- 21. Pyrotechnic fires of the type which occurred on the ORISKANY are almost impossible to control, if they are allowed to reach a magnitude where large masses of combustibles intermixed with their own source of oxygen (sodium nitrate in that disaster) reach their ignition point.

 Instead of permitting the great volume of gases produced to blow-torch

into the ship's interior, there should be separated stowage of pyrotechnic units which vent to overboard. It is interesting to note, that complete extinguishment of a Mk 24 magnesium flare can be easily and safely accomplished by aiming the jet from the water nozzle directly into the burning flame mixture at the end of the flare.

- 22. A constantly recurring fire problem aboard ship involves the inadvertent ignition of deep-fat in frying appliances. Evidence exists that protective high-limit thermostats have failed in certain cases, allowing the fat to reach autoignition temperatures of about 640°F. Some cases of fire in unattended fat fryers not equipped with thermostatic cut-offs have also been reported. A very interesting solution to the extinguishment, control, and quick cooling of these fires has been worked out by NRL. (Report in progress.) Water alone cannot be used to control such fat fires because of the severe frothing problem, and other flame-extinguishing agents do not cool the fat sufficiently to prevent reignition; however, when potassium carbonate solutions are sprayed into the hot fat, saponification ensues. The carbonate solution must also contain a suitable antifoaming agent, in order to attain the cooling action of the water without boiling over fat from the container. It is urged that this extinguishing agent be fleet tested by NAVSHIPSYSCOM in the near future.
- 23. Present methods of instructing shipboard fire fighting personnel need study, revision and modernization. Introduction of new courses of study and devices for developing practical familiarity in handling

do much to increase the readiness and the efficiency of fire fighting teams in ship fire emergencies. Instruction and practice for major fires are badly needed also.

Research and development of more efficient and useful equipment for fighting shipboard fires have always been motivated by "ex post facto" needs. Past catastrophic ship fires prompted immediate shortterm action by naval bureaus which led to installation of almost all of the fire-fighting devices and systems now found on naval vessels. However, once the apparent gap in specific fire protection capability appeared to have been closed, support for R and D on fire fighting systems soon vanished. Newly designed ships have shown evidence that little attention had been given to the redesign and modernization of the old often hastily-designed fire fighting systems. Although the missions of naval vessels and their modes of operations have changed substantially, concurrent changes in shipboard fire protection systems and equipment have not kept pace with new or increased hazards, and this has been especially true of aircraft carriers. More awareness of new advances in R and D on fire fighting methods and their application to shipboard problems on the part of ships' equipment design and allowance authorities needs to be promoted.

Intermediate-Term Recommendations

25. In addition to the utilization of "Light Water" in the vehiclemounted Twinned-Agent Unit for mobile operation on the flight deck and
hangar deck, it would be highly desirable to use "Light Water" in the

High-Capacity Fog-Foam System. However, the present formulation is not fully compatible with seawater. Hence, new formulations containing fluorinated surfactants to further improve "Light Water" and make it more effective with seawater are needed. These are now being investigated by NRL, the 3M Company, and the Dupont Company.

- 26. Further knowledge is required on the behavior of the presently used agents, such as "Light Water" and Purple-K-Powder, under the unusual wind conditions which are normal for the flight deck of aircraft carriers during operations. It is also necessary to determine the best "mix" of agents and techniques for their most efficient application. This program should include investigation of the use of fixed foammaking equipment on the flight deck and the possible use of ships' washdown systems.
- 27. Application of "Light Water" from an airborne helicopter should be investigated further, because it offers good possibilities for reaching into the "pack" of aircraft on the flight deck where access by even hand-pulled handlines is exceedingly awkward and difficult. This concept takes on added feasibility because of the existence of the "angel" helicopter normally hovering immediately off the flight deck during all flight operations. Previous experimental work done by NRL has shown that helicopter application of "Light Water" is highly effective for aircraft fires on land situations (18).
- 28. Exploratory studies are needed to find chemical compounds which are more effective than potassium bicarbonate for quenching fires.

29. Present light-weight, portable, fire pumps operate on highly flammable motor gasoline. Development of portable pumps to operate on a high flash-point fuel would reduce fire hazard. Preferably, the fuel should be JP-5, which is readily available on carriers and most other surface ships. This would also reduce the need for carrying motor gasoline.

Long-Term Recommendations

- 30. Very recently, at the request of the Director of Research of NRL, an NRL Task Force made a study of fire extinguishment research as related to the Navy and its needs. The Task Force also made recommendations for future research at NRL on the subject. The following long-term recommendations stem from the report submitted by that Task Force (19).
- (a) Basic investigations of the film formation, strength, and spreading mechanisms of fluorocarbors on hydrocarbon fuels. (NRL has studies underway in Codes 6040 and 6170 related to this subject.)
- (b) Engineering studies toward superior equipment design of fireextinguishing systems for ship operations.
- (c) Research on new fire-extinguishing agents and techniques, for use in closed or poorly ventilated manned spaces, that are nonhazardous (nontoxic) both per se and as a result of pyrolysis.
- (d) Research on extinguishment of fires involving highly reactive combustibles such as pyrotechnics and propellants.
- (e) Investigations of the use of water-soluble polymers for reducing pressure drop in fire lines and increasing the range of water nozzle

- streams. (NRL, Code 6170, has a current and highly relevant basic research project on drag reduction by water-soluble polymers.)
- (f) Develop more advanced knowledge of the phenomena involved in and required for a flame to propagate. This is highly dependent on the interplay of the physico-chemical and flammability properties of combustibles with each other, with other chemicals, and with their environment, including the nature of the atmosphere they are in. (NRL, Code 6180, has a current and highly relevant research project on ignition and flammability of hydrocarbons and another project on ignition and combustion in unusual atmospheres.)

Conclusion

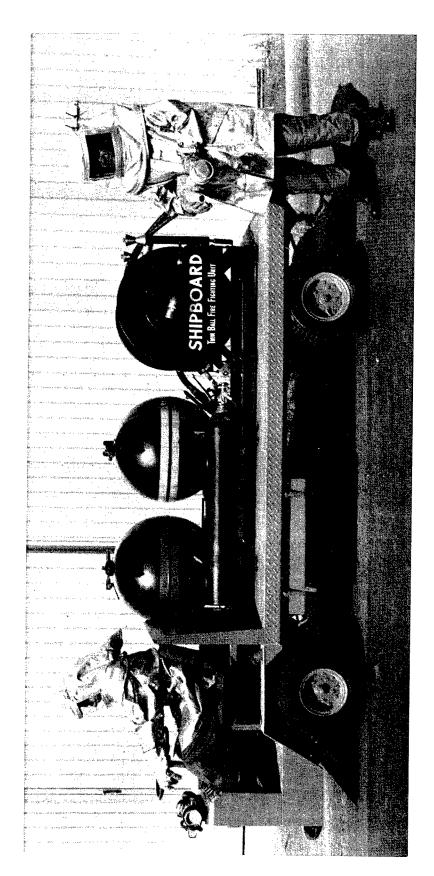
31. It is evident from the findings of the Ad Hoc Task Force (19) that the Navy and NRL have been and are doing a major share of applied research and development in fire extinguishment. However, it is noted there is a minimum effort going on in the Department of Defense in fundamental research in fire extinguishment, of which none is being conducted by the Navy. This is unfortunate, since in the long run the applied aspects of any discipline have so much to gain from the proper understanding and use of fundamental scientific research.

References

- 1. "Fire Fighting Foam Fluid Proportioner--Tests of 60-120 gpm Positive Volume Type," NRL Ltr Rpt N27-8(457)457-58/45, 17 December 1945
- 2. Tuve, R. L., "High Capacity Fog-Foam Fire Fighting Equipment--Final Test and Installation Evaluation of," NRL Ltr Rpt N27-8(46710)834-81/47, 20 June 1947

- 4. Peterson, H. B., Tuve, R. L., "High Capacity Fog-Foam System for Aircraft Carriers, Evaluation Test of," NRL Ltr Rpt 3250-33/49, 15 February 1949
- 5. Peterson, H. B., Jablonski, E. J., Neill, R. R., "Components of High Capacity Fog Foam System for Aircraft Carriers--Evaluation and Design Development of," NRL Ltr Rpt 3250-92/49, 3 August 1949
- 6. Peterson, H. B., Jablonski, E. J., Neill, R. R., "Shipboard High Capacity Fog Foam Fire Fighting Equipment; Proposed Modifications of Proportioner and Analysis of American LaFrance Nozzle," NRL Ltr Rpt 3250 24A/50, 6 February 1950
- 7. Peterson, H. B., "Test and Analysis of Operation of New Dry-Type Fog-Foam System Aboard the USS CORAL SEA (CVB-43)," NRL Ltr Rpt 3250-62A/50, 1 June 1950
- 8. Jablonski, E. J., Tuve, R. L., "Improvement Modification of High Capacity Fog Foam Nozzles; Suggested Accessory for," NRL Ltr Rpt 3250 44A/53, 17 March 1953
- 9. Peterson, H. B., Neill, R. R., Burnett, J. C., "Evaluation of Proposed Fog Foam Proportioner for Shipboard Use," NRL Memo Rpt 287, April 1954
- 10. Specification O-F-555b, "Foam-Forming Liquids, Concentrated Fire Extinguishing, Mechanical," 17 March 1%1
- 11. Jablonski, E. J., Peterson, H. B., Tuve, R. L., "A Study of the Characteristics of Foam-Water Sprinkler Systems in Controlling Full-Scale Fires," NRL Report 5139, 11 June 1958
- 12. Thorson, G. H., Neill, R. R., "Foam Fluid Proportioner, Model 12MP, Hale Fire Pump Company, Conshohocken, Pennsylvania, Test and Evaluation of," NRL Ltr Rpt 3250 43/49, 15 March 1949
- 13. Tuve, R. L., Peterson, H. B., Jablonski, E. J., Neill, R. R., "A New Vapor-Securing Agent for Flammable-Liquid Fire Extinguishment," NRL Rpt 6057, 13 March 1964
- 14. NRL Technical Film Report--"Aircraft Crash Fire Incident Simulation Tests of the Light Water TAU"--ONR-8-64 (Filmed by TID; Text, Direction and Sound Narration by R. L. Tuve.)
- 15. Neill, R. R., "The Hydrocarbon Flame Extinguishing Efficiencies of Sodium and Potassium Bicarbonate Powders," NRL Rpt 5183, 21 August 1958
- 16. Chief of Naval Operations message R22 1204Z of August 1967 to CHNAVMATCOM and CINCPACFLT

- 17. Jablonski, E. J., Peterson, H. B., Tuve, R. L., "A Comparative Testing Study of Fire Extinguishing Agents for Shipboard Machinery Spaces," NRL Memo Rpt 16%, 15 April 1%6
- 18. NRL Technical Film Report--"New Concepts in Rescue and Fire Fighting Using the Helicopter,"--ONR-7-65 (Filmed by TID at Miramar NAS; Text, Direction and Sound Narration by R. L. Tuve.)
- 19. "Report of Ad Hoc Task Force on Fire Extinguishment," 3 August 1967, H. W. Carhart, chairman (Code 6180), W. A. Affens (Code 6180), H. B. Peterson (Code 6040), C. R. Singleterry (Code 6170) and R. L. Tuve (Code 6040), Naval Research Laboratory, Washington, D.C.



SHIPBOARD TWIN-BALL FIRE FIGHTING UNIT

(TBFFU - The "Tee-bee-foo")

A completely self-contained, self-powered, fire extinguishing system developed at the Manned by a single fire fighter, the especially designed nozzle with its 100 feet of hose offers access to fires in hard-to-get-at areas. Pistol grip trigger valves on the dual nozzle gives the fire fighter instantaneous discharge of two of sciences' newest and most powerful fire fighting agents - "LIGHT WATER" and "PURPLE-K-POWDER," Mounted on the Code 0707 line service Naval Research Laboratory for all types of fires on aircraft carrier flight and hangar decks. vehicle shown here, the system can be deployed to fires in seconds of time from positions fore, aft, and at the island of the flight deck. With it, one fire fighter can permanently extinguish over 2,500 square feet of burning fuel in less than 60 seconds.

Section VII. Naval Oxygen Breathing Apparatus (OBA)

by R. R. Miller
Naval Research Laboratory
Washington, D. C.

Introduction

1. In a number of ship disasters where oxygen breathing masks were used, some verbal complaints were made concerning the equipment.

Since NRL developed the potassium superoxide used in the naval oxygen breathing equipment and has an intimate knowledge of the past history and experience with it on shipboard, we are in a good position to discuss the present equipment, its limitations for shipboard use, and its improvement.

Oxygen Breathing Apparatus

2. The emergency oxygen breathing equipment on board the FORRESTAL (CVA 59) is a standard Navy Oxygen Breathing Apparatus (OBA) (Spec. MIL-B-17675B), and the normal allowance for this class of ship is 450 OBA units with six canisters (from either Spec. MIL-C-17671A or Spec. MIL-C-17671C, or both) supplied with each unit. The apparatus is a complete rebreather; i.e., it is sealed from the ambient atmosphere, and the canisters are inserted into it and used one after another depending on how long it is in use. When the mask is being used, the clock-alarm on the OBA is set for 1/2 hour, and when the alarm sounds, the apparatus is checked for breathing bag volume and for ease of exhalation. When both are satisfactory, the clock-alarm is set for an additional 15 minutes, and then the canister is replaced at the end of the 45 minutes of total use. The 2700 canisters on board the FORRESTAL

could thus be used for 3/4 of an hour per canister and, hence, would furnish a total of 2025 man-hours of emergency breathing protection. This means that the available 450 OBA units could have been in simultaneous and continuous use for 4-1/2 hours. An adequate amount of equipment for a major shipboard fire should allow for the possibility that as much as 1/3 is not accessible during such an emergency.

- 3. The average life of a canister for a man operating under normal working conditions is 45 minutes; but if the wearer has an adequate knowledge of the apparatus and its operation, he can adapt and extend the canister life if his activity is more moderate. Thus, under a light working load (for example, standing telephone or machinery watch), he requires less oxygen and produces less carbon dioxide (CO₂), and hence the canister life can be greatly extended. If he is sitting quietly, he reduces the requirement on the canister to such a low value that one canister can furnish the oxygen required and also absorb the CO₂ produced by him for a total of eight hours. At the other extreme, if he must work very hard, he can expend the capacity of the canister in 1/2 hour. Usually that much physical effort would be all he could endure for 1/2 hour. After 1/2 hour of use the canister usually is not exhausted, but its productive capacity has been expended due either to increased resistance to exhalation or to excessive CO₂ in the rebreathed gas.
- 4. The operation of the canister involves a number of chemical reactions taking place in the chemical oxygen source. Water vapor and carbon dioxide from the breath react with the potassium superoxide contained

in the canister, and heat and oxygen are thereby released. It is normal for the reaction to be more efficient and complete as the temperature increases. Best results are obtained if the wearer works at normal rates. The highest work rates produce high enough reaction rates and temperatures sufficient to cause the chemical filling to soften and flow. The material will then develop a blow-hole or compress to offer high breathing resistance. Whenever the canisters are at normal room temperatures or colder, the required reactions of the breath with the superoxide are too slow and inadequate to fulfill the breathing requirement.

5. Two types of canisters were designed and later made available commercially for use in the OBA. They are designated in Navy Spec.

MIL-C-17671A as canister Type I, and in Spec. MIL-C-17671C as canister Type A-3. Type I, the standard canister, requires a starting period of breathing with periodic ventilation of the breathing bags before the level of oxygen production is high enough for breathing purposes. The starting operation becomes completed when the canister has generated sufficient heat as determined by touch (over 100°F). An apparatus taken from stowage at ordinary temperature (68 to 86°F) will require from three to five minutes to start operating adequately for use.

After that, if another standard canister is placed in the used (hot) breathing apparatus, it will operate promptly. The time required in starting the OBA has been criticized for emergency uses where delays can be costly in gaining control of critical fires or in saving lives.

- 6. The Type A-3 canisters, termed quick-start canisters, were designed and manufactured to render the apparatus suitable for immediate use. In this canister, a small oxygen chlorate candle has been placed in the base of an otherwise standard canister. The candle is ignited as soon as the mask is fitted on the operator's face, and the decomposing chlorate candle promptly fills the apparatus with oxygen gas. The chlorate candle burns for about three minutes and supplies nearly ten liters of oxygen during this time; at the same time it warms the canister to a temperature sufficient to maintain reactions with CO₂ and water to support the breathing requirement in the canister. The added cost for quick-start canisters is approximately 1/3 more than the standard canister. This has had a tendency to limit their general use. If necessary, the operator can replace the quick-start canister immediately after it is used up with a standard canister, and his mask will function normally since it will have become well warmed.
- 7. Regardless of the consideration of the cost of such OBA equipment, the expensive phase of the ready-emergency oxygen breathing teams is the training cost. Once a canister has been seated in the apparatus, its diaphragm is punctured, and hence it cannot be stowed thereafter. The time for training each man on an OBA mask does not require that the full life of a canister be consumed, and thus the use of one canister for about four men in breathing training has become the standard practice. Not every man in training has been required to go through the same operation of taking a stowed apparatus and canister and assembling the two for breathing purposes. Where starting candles were used in training,

the ignition of the candle was experienced by only one of the four men. Such incomplete training and the lack of sufficient retraining, the slow starting of standard canisters, and the operator's feeling of being encumbered have been the causes of a number of complaints about the oxygen breathing apparatus.

- 8. However, there are changes already in progress which will improve the efficiency and use of the OBA in the fleet. All canister replacements are Type A-3, the quick-start type, which permit the OBA to be donned and work started at once. A training canister is being developed commercially for Code 6134E of the Naval Ship Systems Command, which, through the use of replaceable parts, can be reused with each trainee performing the same operations as required on the breathing apparatus in service use. Some encumberment is present with any oxygen breathing mask; but the better each man is trained, the less encumbered and more confident he feels. Well-trained personnel accomplish normal operations comfortably with the aid of the OBA, but poorly trained peoplé complain subsequently.
- 9. The chemical oxygen breathing apparatus has several advantages over other types in the greater shelf-life of the equipment and the greater ease the wearer experiences in climbing through small spaces. The existing canisters and candles do not deteriorate under recommended stowage conditions. Oxygen breathing masks which depend on compressed cylinders of oxygen or air are more bulky, are apt to lose pressure during stowage, and depend on sensitive reducing valves which have critical stowage lives.

- 10. One complaint that could be leveled against the chemical OBA is that the usable life of the canisters does not exhaust the chemical filling, as mentioned above. The canisters become unsatisfactory before all the chemical is used, and this accounts for the listed 3/4-hour life of a canister which under average use should last an hour or more.
- 11. We believe that research on the properties of mixtures of potassium superoxide with one of several other oxides could provide sufficient improvement to allow a redesign of the equipment to make the canister more efficient and useful. Past research at NRL on calcium superoxide has been pursued as a very promising approach on new chemical oxygen sources, but work was slowed down several years ago by loss of support from BUSHIPS (Code 632). This support probably ceased due to reorganization and to the glamour of other fields. Resumption of support is urged.

Short-Term Recommendations

- 12. The only way to be able to use oxygen breathing equipment efficiently under critical or disaster conditions is as follows:
 - (a) Train well the men who are most likely to use them.
- (b) Allocate enough OBA's and canisters to each ship to care for large-scale fires.
- (c) Maintain a constant state of readiness of these OBA's and replacement canisters.
- 13. All canisters procured and installed in ships, especially carriers and tankers, should be the quick-start type (Type A-3).

Intermediate-Term Recommendations

- 14. Research on mixed potassium superoxide and other oxides or peroxides should be conducted to search for improvements over the effective performance life of the present potassium superoxide canister filler.
- 15. An investigation of the properties of calcium superoxide, which NRL has already learned to prepare in 60% yields, should be supported to determine if this compound is suitable for use in the oxygen rebreathing apparatus. If the calcium superoxide proves advantageous when used alone or mixed with potassium superoxide, effort should be promptly undertaken to improve the chemical yields of calcium superoxide in order to lower the unit cost and develop a commercial source of supply.

Long-Term Recommendations

- 16. Redesign the OBA to increase efficiency and dependability for longer-life service use and greater convenience to the wearer.
- 17. Investigate new methods for preparing calcium and other alkaline earth superoxides through the ozonide reactions on hydroxides.

Section VIII Toxicity Aspects and Application of the Naval Protective Gas Mask to Shipboard Fires

by Dr. E. A. Ramskill Naval Research Laboratory Washington, D.C.

Toxicity Hazards of Shipboard Fires

- 1. Toxicity hazards associated with a fire are numerous, both in number and degree. Historically, the danger from fire in more or less closed spaces has always been attributed to carbon monoxide (CO) and/or lack of oxygen (O_2) ; this fear is, of course, a real one, but there is more to the overall picture. In the discussion which follows, an attempt is made to separate the hazards from the fire products from those of the fire itself, i.e., heat and flame per se are not considered.
- 2. First, let us consider the "products" of a fire. Of course, the products vary widely depending on the fuel and the conditions. However, when one thinks in terms of a shipboard fire, the fuel includes primarily hydrocarbons, paint, plastics, mattresses, furnishings, and electrical insulation; the conditions, in general, are semiclosed to closed with limited opportunity to go upwind of the fire. The products are those resulting from partial-to-complete oxidation, decomposition and/or evaporation of the myriad of materials present. Notable among the products are carbon dioxide (CO₂), carbon monoxide (CO), hydrogen chloride (HCl), and "smoke"; in addition, there is a lack of oxygen. There are, undoubtedly, thousands of other products, but these are believed to be in relatively small concentrations and/or of low toxicity. There are several compounds which could be added to the above list. For

example, hydrogen fluoride (HF) will, undoubtedly, be formed if Teflon and Teflon-like materials are present. Phosgene can be formed under certain conditions; however, it is rare that tests for phosgene have been positive. The various oxides of nitrogen will be formed when the fuel contains much nitrogen; this situation is rare except in the case of explosives (a special fire situation). The above-mentioned main products of a fire are not normally considered highly toxic, and one wonders why fires are so costly in lives, particularly aboard ship.

- 3. Fatalities from a fire can usually be divided into two distinct categories. For purposes of discussion we shall designate these "immediate" and "delayed." The immediate fatality occurs during the fire; the delayed fatality occurs from 24 to 72 hours after the fire. Each of these categories will be discussed with relation to the probable mechanism of such deaths.
- 4. There are many ways in which a man can be killed in a fire; an injury can prevent his escape, or clothing catching afire can burn him alive. However, the most common means is believed to be a combination of toxic gas and heat—a one-two punch in which the toxic gas knocks the man down and the heat kills him. The toxic gases which can literally knock a man down are CO and lack of oxygen. Actually, the two work together since low oxygen accompanies and enhances the effect of high CO. High CO₂, while not considered toxic, increases the breathing rate and thereby enhances the effect of high CO. The CO may be regarded as the real culprit since concentrations of about 1% act rapidly; O₂ has to be

reduced from 21% to 10-12% before a man collapses from 0_2 deficiency alone. The man may die from high CO or low 0_2 unless he is given fresh air; however, unless he is rescued soon enough, he may become a fatality because of excessive heat. It is believed that most of the pilots lost recently on the ORISKANY died in this way. The reports indicated "peaceful" death due to excessive heat—this means that the men were unconscious (from high CO and/or low 0_2) before heat became excessive.

5. It is interesting at this point to examine data obtained by the National Defense Research Committee during World War II (1) in connection with flame throwers. The pertinent part of their experiments involved gasoline fires in completely enclosed spaces. In each instance the fire extinguished itself, and the air composition after the fire was:

O₂ from 14.5 to 16%
CO₂ from 3.5 to 4.5%
CO from 0.7 to 1.0%

It should be noted that none of these gases, <u>by itself</u>, would knock a man down immediately. However, he would be in distress immediately and probably would go down within a minute from the combination.

6. The data cited above for completely enclosed spaces represents the worst situation for gasoline fires. When other materials are present (paint, plastics, insulation, etc.), it is doubtful that 0₂ will be altered greatly; the proportions of CO₂ and CO may well be altered. Such data have not been located. In all situations, other products are, of course, present, but not all of these have been identified and quantized.

- 7. For spaces which are not completely enclosed, the average composition of the atmosphere can be expected to be less severe to health than cited above. In that case, however, the fire will not extinguish itself and temperatures will increase.
- 8. It is time now for the fire fighter to enter the scene-his purpose, of course, is to extinguish the fire by depriving it of O2 and/or cooling the fuel. Various methods are used, but the classical one is water. When water hits the hot fire, steam is formed and a great dilution of atmospheric gases takes place-the extent depends on the amount of steam generated together with the ventilation rates. Dilution of all the gases is physiologically in the right direction except for O2. This is believed to be the manner in which men are knocked down by low O2. The water used by the fire fighter also plays a part in the next step. NDRC workers showed (2) that dry air at 142°C could be inhaled with relatively little damage. However, if that air was 50% water vapor, the heat liberated in the condensation of the steam in the respiratory tract would cause severe damage. Thus, the water used to combat the fire may well be the most important single factor in causing immediate fatalities.
- 9. Consider now the case of the delayed fatality. In general, this man was in or near the fire and did not sustain injuries or serious burns. He probably did not report to sick bay because he had only a cough and sore lungs from all the smoke he inhaled. But two days later he is dead; the cause is reported "pulmonary edema." He did indeed die of pulmonary edema; but what caused the edema? There are many illustrations of this

type of delayed fatality. One of the most dramatic was the FRANKLIN with nearly 500 men in this category. It is suspected that the FORRESTAL also had more fatalities in this category than in the immediate category; first-day reports gave 25 to 30 fatalities, but three days later the number reported was 130.

- 10. In this case of the delayed fatality one looks for an <u>irritant</u> rather than a <u>toxic</u> compound—one which causes little trouble at the time of the fire but which produces an edema in a day or two. There are, of course, many irritants in the products of a fire, but the one believed to be the main culprit is HCl with a big assist from the smoke. Elkins (3) states that "... phosgene apparently acts by hydrolysis in the lungs with the formation of two molecules of hydrochloric acid. This acid irritates and inflames the lung tissue, which becomes incapable of allowing oxygen to diffuse into the bloodstream. The effects are often delayed..." Elkins also states that concentrations of HCl above 10 parts per million by volume (ppm) are highly irritating. It would appear, therefore, that HCl in the lung is capable of producing a delayed pulmonary edema and that quite low concentrations are very irritating.
- 11. Let us now consider the role which smoke may play in this process of delayed fatalities. For discussion purposes, assume the smoke to be composed of spheres, 10 microns in diameter, and that there are 10⁵ particles per milliliter. This size and concentration of particles is considered reasonable—the exact composition of the particle doesn't matter at this point. The man exposed to this smoke may be fighting the

fire with considerable vigor and hence breathing at a rate up to 50 liters per minute. Now, the total <u>surface area</u> of the particles inhaled per minute is

$$\frac{4\pi(5 \times 10^{-4})^2 \times 10^5 \times 1000 \times 50}{10^4} = 1.5 \text{ square meters of surface area}$$

Inasmuch as this smoke has been in the presence of HCl, assume that the smoke has adsorbed on its surface a monolayer of HCl (a case can be made for <u>more</u> than a monolayer, but there are also competing gases present). An average figure for adsorbed HCl is 35 millimoles per square meter. Hence, the inhaled smoke would contain

$$35 \times 1.5 \times .036 = 1.8 \text{ grams HCl}$$

In order to inhale this much HCl as vapor in one minute at the breathing rate of 50 liters per minute, the concentration would have to be

$$1.8 \times 1000 = 36 \text{ mg HCl/l} = 25,000 \text{ ppm}.$$

It will be recalled that 10 ppm of HCl is "highly irritating," and it is expected that the respiratory system would rebel at 25,000 ppm. However, breathing the above-defined smoke would not be particularly umpleasant—some coughing would probably result, but the respiratory system would accept it. So far, it has been implied that all the smoke inhaled is retained—this, of course, is not the case. A significant portion may be retained, as much as 10 to 50% depending on particle size and density. Once the smoke is deposited on the lung surface, it is reasoned that a large portion of the HCl would be transferred by solution to the lung. In fact, in the high relative humidity of the lung, HCl adsorbed on airborne particles will rapidly absorb water, thus increasing the size and mass of the particle and enhancing deposition.

- 12. There is another means by which HCl can be painlessly carried into the lungs. When water is poured on a fire, large quantities of steam are produced. Near the "edges" of the fire this steam condenses into small water droplets—these droplets will be very effective in absorbing HCl. This aerosol of hydrochloric acid can be inhaled and retained with minor physical discomfort. If it can be shown that HCl is partly or wholly responsible for the delayed effect, treatment with ammonia immediately after the fire could prevent or decrease the effect.
- 13. The above estimates and predictions are subject to experimentation and verification. The estimates may well be no better than an order of magnitude. However, the general mechanism offered for the delayed fatality deserves serious consideration.

Protective Gas Masks

- 14. Protective masks (gas masks) have been carried on all our ships since about 1917. The present model on these ships is the ND-Mk V. In general, these masks have been stowed in damage-control lockers and have been issued only in rare instances. Statements printed on the canisters, on the packages and/or in instruction manuals warn against the use of such masks in oxygen-deficient spaces and where CO may be dangerous. This advice is, of course, based on the facts that the mask does not generate 0₂ and removes only a small amount of CO. Present instructions do not specifically prohibit their use in the vicinity of fires.
- 15. The advisability of using the protective gas mask in and during shipboard fires has been considered on several occasions in the last

- 25 years. Each time the mask's inability to generate 0₂ and remove CO outweighed its then-recognized advantages, and its use in fire fighting was voted down. It is believed that the use of the protective mask in and during shipboard fires should now be reconsidered.
- 16. The role which the protective mask can play in shipboard fires must be clearly defined. It should <u>not</u> be considered a fire fighting item—only as a last resort (all OBA's in use) should it be used for fire fighting proper. However, for the nonparticipant who cannot completely avoid the fire and for escape purposes, the mask should be specified and encouraged. For such a procedure to be successful, the mask would have to be issued and stowed in accessible places, probably at battle stations. Considerable attrition of masks would necessarily occur and some expense thus incurred.
- 17. It is believed that the use of the protective mask for escape and "limited" fire fighting purposes would save many lives. If the mechanism for the delayed fatality described above is correct, all such fatalities would be eliminated by use of the mask. This is true because the mask would remove all of the particulate matter, together with the gases adsorbed thereon, and most (except CO and CO₂) of the gaseous fire products. The mask would also serve to reduce the temperature of hot inhaled air and would constitute a heat shield for the face. Of most importance, of course, would be the absence of pulmonary edema 24 to 72 hours after the fire.
- 18. There is one classical example which enforces the above position. This involved the FRANKLIN in 1945. Nearly 500 men were trapped below

the hangar deck for about 40 hours by multiple fires topside. Many of these men were alive some 24 hours after the fire started, but they were all dead when reached after 40 hours. The exception was a small party of men in one engine room who survived the ordeal with "only a headache." The men in the engine room wore masks all the time; in fact, they wore two—the first became so clogged with smoke that fresh ones were donned. There were no indications that the men who died wore their masks, although masks were available. There are other examples where masks have been used in fires, but none are as dramatic and convincing as the FRANKLIN.

- 19. In recommending the immediate use of protective masks as indicated above, it is realized that sooner or later some well-meaning sailor will misinterpret the instruction and infer that the mask is a substitute replacement for the oxygen breathing apparatus (OBA)—he may use the mask instead of the OBA because it is lighter and much more comfortable. If he encounters high CO and/or low O2, it will be his last mistake, and the mask will be blamed. However, for every man lost by mistake this way, perhaps ten will be saved by preventing the delayed effects.
- 20. It is fully appreciated that limited use of the protective mask is not a perfect solution to the loss of life from shipboard fires. However, it is believed to be a good solution which will save lives and perhaps, most important, the procedure can be put into effect today because the masks are aboard now.

Short-Term Recommendation

21. It is recommended that the use of the protective mask (ND-Mk V) be specified and encouraged for escape and limited fire fighting purposes at the earliest practicable time. No experimental work is required.

Intermediate-Term Recommendations

- 22. It is recommended that experimental work be conducted to:
- (a) Determine the nature and amount of fire products from such materials as paint, electrical insulation, etc., under closed and semi-closed conditions.
- (b) Determine the irritant and/or toxic gas carrying potential of various particulates with emphasis on those produced by fires.
- (c) Determine the most practical devices and procedures to protect shipboard personnel from the toxicological effects of fires.

Long-Term Recommendation

23. It is recommended that the physiological effect of various typical fire atmospheres be determined with emphasis on the mechanism of physiological damage. This is probably long-term work, although portions could be short- and intermediate-term work. This work should be done by the Naval Medical Research Institute or the Naval Toxicology Unit, both in Bethesda, Maryland.

References

- 1. Summary Technical Report of NDRC, Division 9, Vol. 1, p. 305, 1946.
- 2. Summary Technical Report of NDRC, Division 9, Vol. 1, p. 323, 1946.
- 3. H. B. Elkins, Chemistry of Industrial Toxicology, Wiley, 1950.